# ANNUAL PROGRAM REVIEW

# CHEMICAL PULPING AND BLEACHING

March 24-25, 1998

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March 24-25, 1998

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Revised 02/03/98:at

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# ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED CHEMICAL PULP

Status Report for Project F013

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Arthur J. Ragauskas
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Nidhi Rawat
Jean-Christophe Baromés
Blair Carter
Narendra Patel
Mark Turner

March 24-25, 1998

## DUES-FUNDED PROJECT SUMMARY

## FY 1997-98

| | |
|---|---|
| **Date:** | March 10, 1998 |
| **Project Title:** | Environmentally Compatible Production of Bleached Chemical Pulp |
| **Project Code:** | BLECH |
| **Project Number:** | F013 |
| **PAC:** | Chemical Pulping and Bleaching |
| **Division:** | Chemical and Biological Sciences |
| **Project Staff** | |
| **Faculty/Senior Staff:** | T.J. McDonough, C.E. Courchene, A. Ragauskas |
| **Staff:** | A. Shaket, N. Rawat, J.-C. Baromès, B. Carter, N. Patel, M. Turner |
| **FY 97-98 Budget:** | $297,401 |
| **Allocated as Matching Funds:** | |
| **Project 4201:** | $26,191 |
| **Project 4159:** | 8,681 |
| **Project 4120:** | 32,576 |
| **Project 4106:** | 5,000 |
| **Time Allocation** | |
| **Faculty/Senior Staff:** | 0.9 |
| **Support:** | 1.25 |
| **Supporting Research** | |
| **M.S. Students:** | Aric Bacon, Carter Johnson |
| **Ph.D. Students:** | See F015 |
| **External:** | Project 4201, "Bleach Plant Capital Reduction with Rapid $D_0$ and Simplified Bleaching" (U.S. D.O.E Agenda 2020 Capital Effectiveness) |
| | Project 4159, "High Efficiency $ClO_2$ Delignification" (U.S. D.O.E. Agenda 2020 Environmental) |
| | Project 4120 "Energy Efficient Kraft Pulping for Highly Bleachable, Low Lignin Content Pulp" (U.S. D.O.E. Paper Mill of the Future) |
| | Project 4106, "An Integrated Approach to Bleaching and Secondary Treatment Systems for Prevention of Pollution by Chloro-organics" (Georgia Consortium for Technological Competitiveness - Project now terminated) |

**RESEARCH LINE/ROADMAP:** Environmental Performance/RM5 - Reduce Emissions

**PROJECT OBJECTIVE:**

Define pulping and bleaching technology that will decrease or eliminate the release of byproduct organic chlorine compounds without sacrificing bleached pulp quality.

**PROJECT BACKGROUND:**

Previous work has included research on the relationship between pulping conditions and bleachability, improvements to elemental chlorine free (ECF) bleaching sequences, chlorine compound free delignification and bleaching and characterization of bleach filtrates with regard to potential for environmental effect. Previous work on relating softwood pulping conditions to bleachability investigated the effects of effective alkali (EA) charge, sulfidity and anthraquinone. In the $D_0(EO)D_1$ sequence, increasing EA increases brightness ceiling and decreases the amount of $ClO_2$ needed for a given brightness, while decreasing the kappa number has a similar effect. Effects of EA after full bleaching are more subtle. At normal unbleached kappa numbers, increasing EA increases the brightness ceiling. Addition of anthraquinone (AQ) had a barely noticeable negative effect on the brightness ceiling, but soda and soda-AQ pulps had significantly (2-3 points) lower brightness ceiling than the corresponding kraft and kraft-AQ pulps. Earlier research directed toward improved $ClO_2$ - based ("elemental chlorine free," ECF) bleaching sequences has been centered on two objectives: (1) defining the benefits of a very short retention time chlorine dioxide delignification ("$D_0$") stages and (2) analyzing ECF bleaching process behavior as a route to higher bleaching efficiency and better environmental performance. This work has demonstrated the potential of short retention time $D_0$ stages to reduce capital investment and formation of chlorinated organic byproducts. The objectives of earlier research done on nonchlorine delignification and bleaching were (1) to determine the kinetics of delignification and carbohydrate attack by ozone, as a route toward ozone bleaching systems having improved selectivity and (2) to investigate delignification by combinations of oxygen and hydrogen peroxide in the presence of potentially beneficial additives (cyanamide, DTMPA and $MgSO_4$). Research on environmental effects of bleaching filtrates was done in the form of Ph.D. thesis research on the toxicity of filtrates from chlorine and chlorine dioxide delignification sequences after oxygen delignification. A general conclusion was that, by most assays, the chlorine dioxide filtrates were not significantly toxic. The toxicity revealed by more sensitive assays appeared to not to originate in the bleaching stages and was attenuated at higher oxidant charges.

The resources available to this project have been effectively leveraged through external funding by the U.S. Department of Energy and, to a lesser extent, the Georgia Consortium for Technological Competitiveness in Pulp and Paper. Project F013 has contributed a limited amount of matching funds to each of four projects, each of which has goals that are closely aligned with those of Project F013.

During the period March, 1997 - February, 1998, our research efforts have included the following:

- Peroxide bleaching of softwood kraft pulps produced under systematically varied kraft pulping conditions.
- Comparative analysis of $(DC)(EO)D_1$ and $D_0(EO)D_1$ bleaching sequences, with respect to effects of kappa factor (KF), effluent carryover and pH in the $D_1$ stage.
- Initiation of a study of the effects of oxygen delignification and ECF bleaching on pulp physical properties.
- Mill-scale evaluation of "Rapid $D_0$" bleaching (with Project 4201).
- Rapid $D_0$ bleaching of simulated "Lo-Solids®" and conventional kraft pulps at normal and low kappa numbers (with Project 4159).
- Gas phase bleaching of conventional and simulated RDH pulps from hardwoods and softwoods (with Project 4159).
- ECF bleaching of softwood pulps from controlled liquor concentration profile kraft cooks (with Project 4120).

- Bleachability of birch and maple pulps prepared under different conditions of alkali charge and temperature (with Project 4120).
- Effects of washer efficiency on characteristics of effluents from d(epo)d bleaching of a softwood kraft pulp (with Project 4120).

## SUMMARY OF RESULTS:

We have conducted a variety of investigations in the area of environmentally compatible manufacture of bleached chemical pulp. These have included studies of peroxide delignification of kraft pulps, ECF bleaching process behavior, effects of kraft, oxygen and $ClO_2$ delignification on pulp physical properties, Rapid $D_0$ mill trials and laboratory studies, vapor phase $ClO_2$delignification, effects of cooking liquor concentration profiling on bleachability, effects of pulping conditions on hardwood bleachability, and effects of bleach plant washer inefficiency on effluent characteristics.

We have shown that modern chelation-peroxide technology is capable of extensively delignifying southern pine kraft brownstock produced under a wide variety of pulping conditions and over wide range of kappa numbers. The unbleached brightness of the pulps increases with decreasing kappa number and increasing EA charge, and may also be positively affected by increased cooking temperature and negatively affected by increased liquor-to-wood ratio. The decrease in kappa number upon chelation followed by peroxide treatment increases with increasing unbleached kappa number. The corresponding decrease in chromophore content, as measured by the observed decrease in k/s, is higher for high kappa number pulps, especially when those pulps were produced with a low EA charge. There may also be a negative effect of high alkali charge, a beneficial effect of high liquor-to-wood ratio, and negative effect of maximum cooking temperature.

In a comparison of effects of carryover and $D_1$ stage pH in ECF and (DC)-based bleaching, we have shown that carryover increases the (EO) kappa number under a variety of conditions of substitution and kappa factor (KF). At low KF, carryover has about the same effect on $D_0$ and (DC) bleaching. However, at high KF, carryover has significantly less effect on $D_0$ than on (DC). It is hypothesized that this is due to the presence, in the dissolved organic black liquor solids, of a fraction that is unreactive toward $ClO_2$ but reactive toward $Cl_2$. Final brightness is higher for $D_0$ than for (DC) when carryover is high, and the optimum $D_1$ exit pH is higher at low KF than at high KF, and higher in the presence of carryover than in its absence, both of these effects being greater for ECF than for bleaching at the lower substitution level.

A joint project between the Chemical and Biological Sciences (CBSD) and Fiber and Paper Physics (FPPD) Divisions has been initiated to characterize the effects of delignification and bleaching processes on fiber properties. The initial work has been defined to include conventional kraft batch pulping, oxygen delignification, and both CED and DED bleaching. Kraft pulps from southern pine chips have been prepared at Kappa nos. of 94, 29, and 17and selected pulps have been further delignified by medium-consistency oxygen as described below. The 29 and 17 Kappa pulps and the oxygen delignified pulps will be bleached with both CED and DED sequences. The extent of fiber property and strength changes imparted by the delignification and bleaching processes will be examined by FPPD.

In a mill trial of the Rapid $D_0$ concept, samples were taken immediately downstream of mixers in which $ClO_2$ was added to unbleached pine kraft in a full scale operating bleach plant. Analysis of the samples showed that retention times of 30, 60 and 120 seconds gave, after extraction, 87, 90 and 92% of the delignification achieved in the mill's $ClO_2$ delignification ($D_0$) and extraction stages, each of which has a retention time of approximately one hour. It was concluded that the industrial scale mixers, both static and dynamic, can give sufficiently good mixing to make Rapid $D_0$ bleaching industrially feasible.

Laboratory studies have shown that Rapid $D_0$ bleaching is applicable to conventional and Lo-Solids® pulps and to pulps prepared at unusually low kappa number levels. Unlike conventional $ClO_2$ delignification, Rapid $D_0$ delignification does not consume more active chlorine per unit of lignin removed as the unbleached kappa number is decreased.

Laboratory vapor phase $ClO_2$ delignification experiments were performed on hardwood pulps made from sweetgum by laboratory simulations of both conventional and RDH kraft pulping. A smaller number of experiments were conducted on pulps made from southern pine by laboratory simulations of conventional kraft pulping. All experiments consisted of $D_0$(EO) bleaching followed by determinations of kappa number and analysis of the individual stage filtrates for AOX, as well as chloride, chlorate and chlorite ions. For comparison, control experiments were done in which the $ClO_2$ was applied at low consistency, in the conventional manner. In bleaching the hardwood pulps, vapor phase delignification was remarkably more efficient, but generated markedly larger quantities of AOX than the conventional process, which itself generated much more AOX than expected on the basis of earlier softwood pulp bleaching data. These observations, together with analyses of the bleaching filtrates, are consistent wit the hypothesis that $ClO_2$ partially decomposes to $Cl_2$ in the vapor phase before reacting with the pulp. In the case of southern pine kraft pulps, there was a much smaller improvement in delignification efficiency in going from low consistency to vapor phase bleaching. Qualitatively similar observations were made with regard to the softwood pulps, but the trends were generally less pronounced than in the case of the hardwood pulps. Differences in the structure of hardwood pulp residual lignin after conventional and vapor phase bleaching were slight. This may indicate that the superior bleaching efficiency of the vapor phase process is due to diminished importance of reactions that occur between active chlorine compounds and dissolved organic byproducts.

In an effort to assign a cause for the superior bleachability of pulps made by modified pulping processes, we have conducted systematic bleaching studies of southern pine pulps prepared with two types of controlled liquor concentration profiles. In one type, the alkali concentration, after an initial decrease, was maintained at a constant value. In the second type, the same kind of alkali profile was augmented by continuous liquor replacement to limit the concentrations of dissolved lignin and other reaction products. Neither type of profiling had any effect on the bleachability of the resulting pulps in the $D_0$(EO)$D_1E_2D_2$ bleaching sequence. Structural analyses of residual lignins showed that alkali profiled cooks gave residual lignins having slightly lower contents of phenolic groups, both uncondensed and condensed, as well as lower contents of aliphatic hydroxyl groups. These differences may contribute to the failure of the pulps from the profiled cooks to exhibit better bleachability than those from conventional cooks

We have conducted a systematic study of AOX, BOD, and COD released by bleaching southern pine kraft pulp in the $D_0$(EPO)$D_1$ sequence at a kappa factor of 0.20 and a $D_1$ stage $ClO_2$ charge of 1.2%. Measurements of all three parameters were made at three different levels of carryover of $D_0$ stage filtrate into the (EPO) stage and three different levels of carryover of (EPO) stage effluent into the $D_1$ stage, and the entire experiment was duplicated. The combined AOX contributions of the $D_0$ and (EPO) stages amounted to 11.6% of the chlorine atoms applied in the $D_0$ stage, while the contribution of the $D_1$ stage amounted to 2.7% of the chlorine atoms applied in the $D_1$ stage. The combined AOX contributions of all three stages decreased when the $D_0$ stage carryover was increased from 0 to 10% and was unaffected by (EPO) stage carryover. With perfect washing between stages, COD contributions to the combined bleach plant filtrates by the $D_0$, (EPO) and $D_1$ stages were, respectively, 14.1, 39.8, and 2.9 kg/odumt. The combined COD contributions of all three stages was relatively unaffected by a low level (5%) of $D_0$ stage carryover, but a higher level (10%) resulted in an overall COD increase of 2 kg/odumt. Increasing (EPO) stage carryover from 0 to 30% decreased total COD by 3 kg/t. With perfect washing between stages, BOD contributions to the combined bleach plant filtrates by the $D_0$, (EPO), and $D_1$ stages were, respectively, 3.8, 7.0, and 2.2 kg/odumt. No significant effect of carryover levels on the total BOD release could be detected.

The results of hardwood bleachability studies indicate that the EA and pulping temperature affect the nature and bleachability of the pulp produced. An important outcome of this work was that high EA and high temperature pulping emerged as a very attractive option for maple. High EA pulping significantly reduces the cooking time and produces brighter pulps at practically comparable pulp yield and viscosity. It also greatly enhances maple pulp bleachability by producing very high brightness pulps in only 3 stages of ECF bleaching. For birch, high EA has a negative effect on pulp yield and viscosity although it greatly improves the bleaching response in ECF bleaching sequence. However, high temperature is somewhat better for birch in that it produces high brightness pulps with less $ClO_2$ consumption with insignificant effect on pulp yield and viscosity.

**GOALS FOR FY 97-98:**

1. Complete a study of effects of delignification with kraft pulping liquor, oxygen, chlorine and chlorine dioxide on pulp refining behavior and fiber properties.
2. Prepare or otherwise acquire a set of softwood and hardwood pulps representing a wide range of bleachabilities and use them to evaluate a defined set of candidate predictors of ease of delignification by (1) an oxygen stage and (2) a D(EO) sequence at several extents of delignification.
3. Complete a response surface study of the relationship between kraft pulping variables and ease of removal of lignin by oxygen and peroxide stages.
4. Determine optimum conditions for the chlorine dioxide brightening stages in ECF bleaching of softwood and hardwood kraft pulps.
5. Confirm benefits of short retention time chlorine dioxide delignification on the mill scale.
6. Report laboratory work to date on short retention time chlorine dioxide delignification

**DELIVERABLES FOR FY 97-98:**

Study of effects of delignification with kraft pulping liquor, oxygen, chlorine and chlorine dioxide on pulp refining behavior and fiber properties.

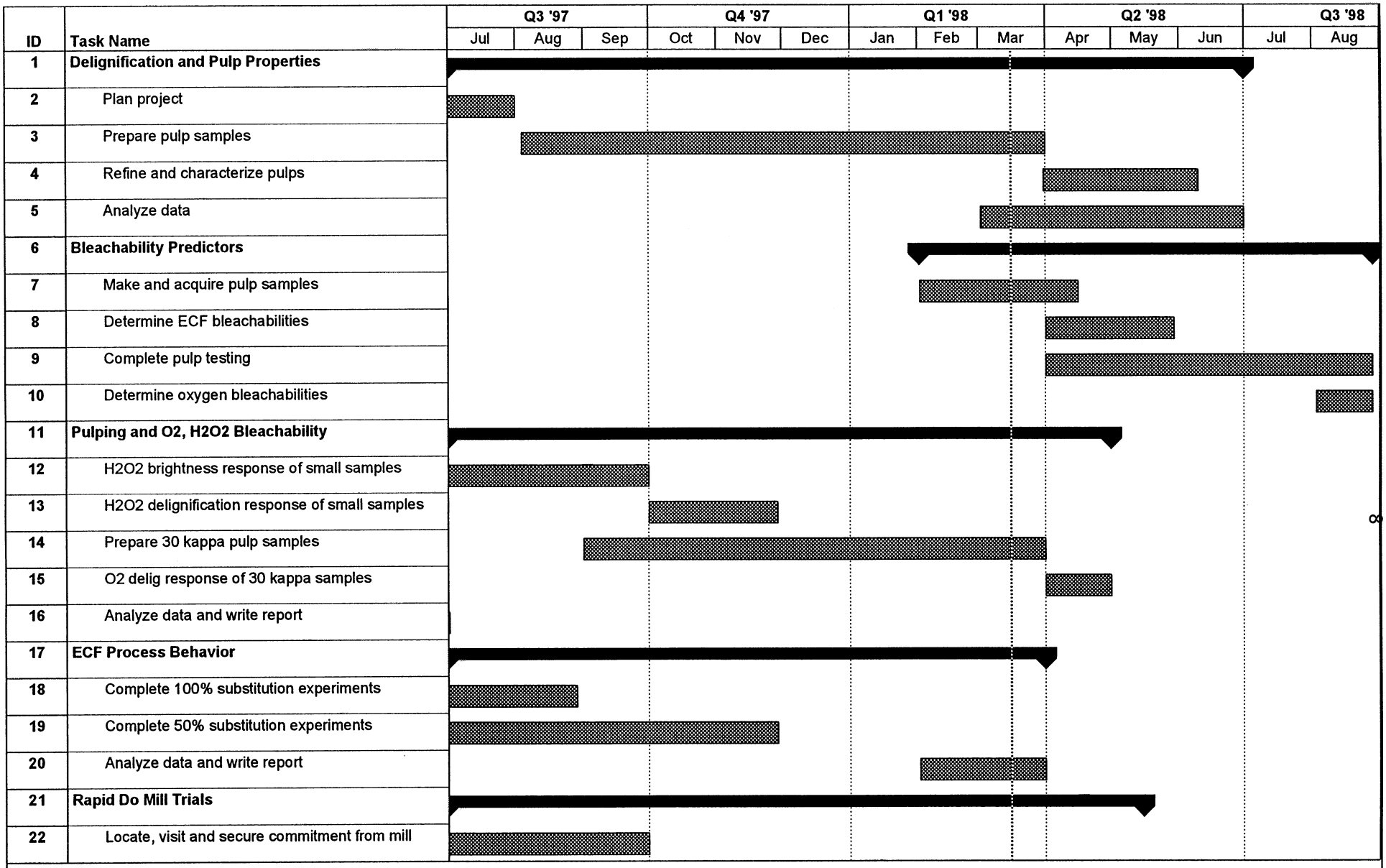
Evaluation of a defined set of candidate predictors of ease of delignification by (1) an oxygen stage and (2) a D(EO) sequence at several extents of delignification.

Response surface study of the relationship between kraft pulping variables and ease of removal of lignin by an oxygen stage

Confirmation of benefits of short retention time chlorine dioxide delignification on the mill scale.

Report of laboratory work to date on short retention time chlorine dioxide delignification.

**SCHEDULE** (Attach Timeline):


Q3 '97
Q4 '97
Q1 '98
Q2 '98
Q3 '98
Jul
Aug
Sep
Oct
Nov
Dec
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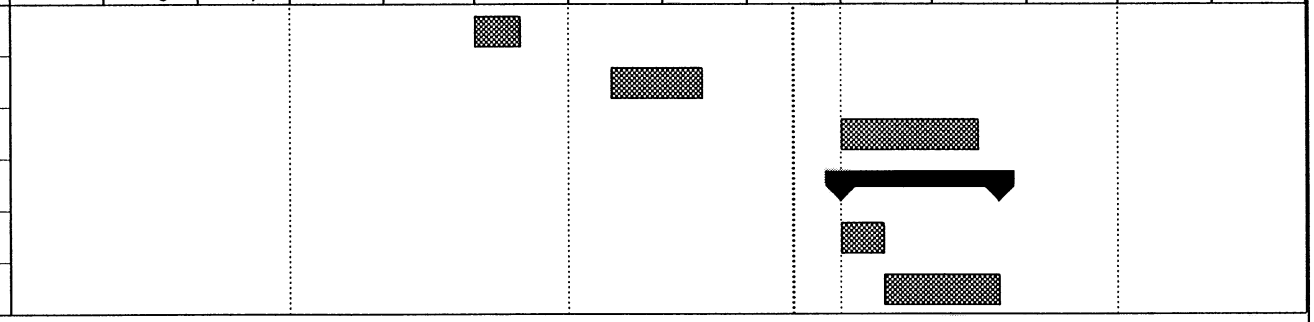
Apr
May
Jun
Jul
Aug
ID
Task Name
1 Delignification and Pulp Properties
2 Plan project
3 Prepare pulp samples
4 Refine and characterize pulps
5 Analyze data
6 Bleachability Predictors
7 Make and acquire pulp samples
8 Determine ECF bleachabilities
9 Complete pulp testing
10 Determine oxygen bleachabilities
11 Pulping and O2, H2O2 Bleachability
12 H2O2 brightness response of small samples
13 H2O2 delignification response of small samples
14 Prepare 30 kappa pulp samples
15 O2 delig response of 30 kappa samples
16 Analyze data and write report
17 ECF Process Behavior
18 Complete 100% substitution experiments
19 Complete 50% substitution experiments
20 Analyze data and write report
21 Rapid Do Mill Trials
22 Locate, visit and secure commitment from mill
Project: 803F013A
Date: Mon 3/16/98
Task
Progress
Milestone
Summary
Rolled Up Task
Rolled Up Milestone
Rolled Up Progress

| ID | Task Name |
|---|---|
| 23 | Prepare and have mill approve plan |
| 24 | Complete SW sampling, analysis and data analysi |
| 25 | Complete HW sampling, analysis and data analysi |
| 26 | **Rapid Do Report** |
| 27 | Assemble data |
| 28 | Complete report |






Project: 803F013A
Date: Mon 3/16/98

Task
Progress
Milestone
Summary
Rolled Up Task
Rolled Up Milestone
Rolled Up Progress

# Project F013

# Environmentally Compatible Production of Bleached Chemical Pulp

**March , 1998**

## Summary

We have conducted a variety of investigations in the area of environmentally compatible manufacture of bleached chemical pulp. These have included studies of peroxide delignification of kraft pulps, ECF bleaching process behavior, effects of kraft, oxygen and $ClO_2$ delignification on pulp physical properties, Rapid $D_0$ mill trials and laboratory studies, vapor phase $ClO_2$delignification, effects of cooking liquor concentration profiling on bleachability, effects of pulping conditions on hardwood bleachability, and effects of bleach plant washer inefficiency on effluent characteristics.

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In a comparison of effects of carryover and $D_1$ stage pH in ECF and (DC)-based bleaching, we have shown that carryover increases the (EO) kappa number under a variety of conditions of substitution and kappa factor (KF). At low KF, carryover has about the same effect on $D_0$ and (DC) bleaching. However, at high KF, carryover has significantly less effect on $D_0$ than on (DC). It is hypothesized that this is due to the presence, in the dissolved organic black liquor solids, of a fraction that is unreactive toward $ClO_2$ but reactive toward $Cl_2$. Final brightness is higher for $D_0$ than for (DC) when carryover is high, and the optimum $D_1$ exit pH is higher at low KF than at high KF, and higher in the presence of carryover than in its absence, both of these effects being greater for ECF than for bleaching at the lower substitution level.

A joint project between the Chemical and Biological Sciences (CBSD) and Fiber and Paper Physics (FPPD) Divisions has been initiated to characterize the effects of delignification and bleaching processes on fiber properties. The initial work has been defined to include conventional kraft batch pulping, oxygen delignification, and both CED and DED bleaching. Kraft pulps from southern pine chips have been prepared at Kappa nos. of 94, 29, and 17and selected pulps have been further delignified by medium-consistency oxygen as described below. The 29 and 17 Kappa pulps and the oxygen delignified pulps will be bleached with both CED and DED sequences. The extent of fiber property and strength changes imparted by the delignification and bleaching processes will be examined by FPPD.

In a mill trial of the Rapid $D_0$ concept, samples were taken immediately downstream of mixers in which $ClO_2$ was added to unbleached pine kraft in a full scale operating bleach plant. Analysis of the samples showed that retention times of 30, 60 and 120 seconds gave, after extraction, 87, 90 and 92% of the

delignification achieved in the mill's $ClO_2$ delignification ($D_0$) and extraction stages, each of which has a retention time of approximately one hour. It was concluded that the industrial scale mixers, both static and dynamic, can give sufficiently good mixing to make Rapid $D_0$ bleaching industrially feasible.

Laboratory studies have shown that Rapid $D_0$ bleaching is applicable to conventional and Lo-Solids® pulps and to pulps prepared at unusually low kappa number levels. Unlike conventional $ClO_2$ delignification, Rapid $D_0$ delignification does not consume more active chlorine per unit of lignin removed as the unbleached kappa number is decreased.

Laboratory vapor phase $ClO_2$ delignification experiments were performed on hardwood pulps made from sweetgum by laboratory simulations of both conventional and RDH kraft pulping. A smaller number of experiments were conducted on pulps made from southern pine by laboratory simulations of conventional kraft pulping. All experiments consisted of $D_0$(EO) bleaching followed by determinations of kappa number and analysis of the individual stage filtrates for AOX, as well as chloride, chlorate and chlorite ions. For comparison, control experiments were done in which the $ClO_2$ was applied at low consistency, in the conventional manner. In bleaching the hardwood pulps, vapor phase delignification was remarkably more efficient, but generated markedly larger quantities of AOX than the conventional process, which itself generated much more AOX than expected on the basis of earlier softwood pulp bleaching data. These observations, together with analyses of the bleaching filtrates, are consistent wit the hypothesis that $ClO_2$ partially decomposes to $Cl_2$ in the vapor phase before reacting with the pulp. In the case of southern pine kraft pulps, there was a much smaller improvement in delignification efficiency in going from low consistency to vapor phase bleaching. Qualitatively similar observations were made with regard to the softwood pulps, but the trends were generally less pronounced than in the case of the hardwood pulps. Differences in the structure of hardwood pulp residual lignin after conventional and vapor phase bleaching were slight. This may indicate that the superior bleaching efficiency of the vapor phase process is due to diminished importance of reactions that occur between active chlorine compounds and dissolved organic byproducts.

In an effort to assign a cause for the superior bleachability of pulps made by modified pulping processes, we have conducted systematic bleaching studies of southern pine pulps prepared with two types of controlled liquor concentration profiles. In one type, the alkali concentration, after an initial decrease, was maintained at a constant value. In the second type, the same kind of alkali profile was augmented by continuous liquor replacement to limit the concentrations of dissolved lignin and other reaction products. Neither type of profiling had any effect on the bleachability of the resulting pulps in the $D_0$(EO)$D_1E_2D_2$ bleaching sequence. Structural analyses of residual lignins showed that alkali profiled cooks gave residual lignins having slightly lower contents of phenolic groups, both uncondensed and condensed, as well as lower contents of aliphatic hydroxyl groups. These differences may contribute to the failure of the pulps from the profiled cooks to exhibit better bleachability than those from conventional cooks

We have conducted a systematic study of AOX, BOD, and COD released by bleaching southern pine kraft pulp in the $D_0$(EPO)$D_1$ sequence at a kappa factor of 0.20 and a $D_1$ stage $ClO_2$ charge of 1.2%. Measurements of all three parameters were made at three different levels of carryover of $D_0$ stage filtrate into the (EPO) stage and three different levels of carryover of (EPO) stage effluent into the $D_1$ stage, and the entire experiment was duplicated. The combined AOX contributions of the $D_0$ and (EPO) stages amounted to 11.6% of the chlorine atoms applied in the $D_0$ stage, while the contribution of the $D_1$ stage amounted to 2.7% of the chlorine atoms applied in the $D_1$ stage. The combined AOX contributions of all three stages decreased when the $D_0$ stage carryover was increased from 0 to 10% and was unaffected by (EPO) stage carryover. With perfect washing between stages, COD contributions to the combined bleach plant filtrates by the $D_0$, (EPO) and $D_1$ stages were, respectively, 14.1, 39.8, and 2.9 kg/odumt. The combined COD contributions of all three stages was relatively unaffected by a low level (5%) of $D_0$ stage carryover, but a higher level (10%) resulted in an overall COD increase of 2 kg/odumt. Increasing (EPO) stage carryover from 0 to 30% decreased total COD by 3 kg/t. With perfect washing between stages, BOD contributions to the combined bleach plant filtrates by the $D_0$, (EPO), and $D_1$ stages were, respectively, 3.8, 7.0, and 2.2 kg/odumt. No significant effect of carryover levels on the total BOD release could be detected.

The results of hardwood bleachability studies indicate that the EA and pulping temperature affect the nature and bleachability of the pulp produced. An important outcome of this work was that high EA and high temperature pulping emerged as a very attractive option for maple. High EA pulping significantly reduces the cooking time and produces brighter pulps at practically comparable pulp yield and viscosity. It also greatly enhances maple pulp bleachability by producing very high brightness pulps in only 3 stages of ECF bleaching. For birch, high EA has a negative effect on pulp yield and viscosity although it greatly improves the bleaching response in ECF bleaching sequence. However, high temperature is somewhat better for birch in that it produces high brightness pulps with less $ClO_2$ consumption with insignificant effect on pulp yield and viscosity.

## Introduction

The overall objective of this project is to define pulping and bleaching technology that will decrease or eliminate the release of byproduct organic chlorine compounds without sacrificing bleached pulp quality.

Previous work has included research on the relationship between pulping conditions and bleachability, improvements to elemental chlorine free (ECF) bleaching sequences, chlorine compound free delignification and bleaching and characterization of bleach filtrates with regard to potential for environmental effect. Previous work on relating softwood pulping conditions to bleachability investigated the effects of effective alkali (EA) charge, sulfidity and anthraquinone. In the $D_0(EO)D_1$ sequence, increasing EA increases brightness ceiling and decreases the amount of $ClO_2$ needed for a given brightness, while decreasing the kappa number has a similar effect. Effects of EA after full bleaching are more subtle. At normal unbleached kappa numbers, increasing EA increases the brightness ceiling. Addition of anthraquinone (AQ) had a barely noticeable negative effect on the brightness ceiling, but soda and soda-AQ pulps had significantly (2-3 points) lower brightness ceiling than the corresponding kraft and kraft-AQ pulps. Earlier research directed toward improved $ClO_2$ - based ("elemental chlorine free," ECF) bleaching sequences has been centered on two objectives: (1) defining the benefits of a very short retention time chlorine dioxide delignification ("$D_0$") stages and (2) analyzing ECF bleaching process behavior as a route to higher bleaching efficiency and better environmental performance. This work has demonstrated the potential of short retention time $D_0$ stages to reduce capital investment and formation of chlorinated organic byproducts. The objectives of earlier research done on nonchlorine delignification and bleaching were (1) to determine the kinetics of delignification and carbohydrate attack by ozone, as a route toward ozone bleaching systems having improved selectivity and (2) to investigate delignification by combinations of oxygen and hydrogen peroxide in the presence of potentially beneficial additives (cyanamide, DTMPA and $MgSO_4$). Research on environmental effects of bleaching filtrates was done in the form of Ph.D. thesis research on the toxicity of filtrates from chlorine and chlorine dioxide delignification sequences after oxygen delignification. A general conclusion was that, by most assays, the chlorine dioxide filtrates were not significantly toxic. The toxicity revealed by more sensitive assays appeared to not to originate in the bleaching stages and was attenuated at higher oxidant charges.

The resources available to this project have been effectively leveraged through external funding by the U.S. Department of Energy and, to a lesser extent, the Georgia Consortium for Technological Competitiveness in Pulp and Paper. Project F013 has contributed a limited amount of matching funds to each of four projects, each of which has goals that are closely aligned with those of Project F013. The projects are

- Project 4201, "Bleach Plant Capital Reduction with Rapid $D_0$ and Simplified Bleaching"
- Project 4159, "High Efficiency $ClO_2$ Delignification"
- Project 4120 "Energy Efficient Kraft Pulping for Highly Bleachable, Low Lignin Content Pulp"
- Project 4106, "An Integrated Approach to Bleaching and Secondary Treatment Systems for Prevention of Pollution by Chloro-organics."

During the current reporting period (March, 1997 - February, 1998) our research efforts have included the following:

- Peroxide bleaching of softwood kraft pulps produced under systematically varied kraft pulping conditions.
- Comparative analysis of (DC)(EO)$D_1$ and $D_0$(EO)$D_1$ bleaching sequences, with respect to effects of kappa factor (KF), effluent carryover and pH in the $D_1$ stage.
- Initiation of a study of the effects of oxygen delignification and ECF bleaching on pulp physical properties.
- Mill-scale evaluation of "Rapid $D_0$" bleaching (with Project 4201).
- Rapid $D_0$ bleaching of simulated "Lo-Solids®" and conventional kraft pulps at normal and low kappa numbers (with Project 4159).
- Gas phase bleaching of conventional and simulated RDH pulps from hardwoods and softwoods (with Project 4159).
- ECF bleaching of softwood pulps from controlled liquor concentration profile kraft cooks (with Project 4120).
- Bleachability of birch and maple pulps prepared under different conditions of alkali charge and temperature (with Project 4120).
- Effects of washer efficiency on characteristics of effluents from d(epo)d bleaching of a softwood kraft pulp (with Project 4120).

This report summarizes the results of each of these activities.

# Kraft Pulping Conditions and Peroxide Bleachability

## *Introduction*

Previous work has shown that kraft pulp bleachability is affected by changing certain pulping variables while holding all others constant. . In the $D_0$(EO)$D_1$ sequence, increasing EA increases brightness ceiling and decreases the amount of $ClO_2$ needed for a given brightness. Soda pulps are more difficult to bleach than kraft, suggesting that bleachability may be affected by changing the sulfidity during kraft cooking. In recent work, described below, we have shown that hardwood kraft pulp bleachability is affected by temperature. There is less known about the effects of making simultaneous changes in various combinations of variables, on either $ClO_2$or oxygen bleachability. Accordingly an M.S. student project was undertaken by Mr. Aric Bacon to systematically study the effects of pulping variables and their interactions on ease of delignification by oxygen. The first task in this project was to determine the H-factor values required to prepare pulps having the same unbleached kappa number under a wide variety of conditions of liquor-to-wood ratio, effective alkali charge, sulfidity and temperature. To do this, a response surface experiment was conducted in which the variables included the four already mentioned as well as a fifth, target kappa number. A range of target kappa numbers was selected, and an existing empirical southern pine kraft pulping model was used to calculate the needed H-factor at each of the required combinations of levels of the other four variables. These were used to carry out the pulping runs dictated by the response surface experimental design, and the deviations of the actual kappa numbers from the target values, were used to calculate corrected H-factors for use in the final experiments, which are in progress at the time of writing.

In the meantime, however, the initial response surface design had made available a large collection of unbleached pulps representing a wide variety of pulping conditions. They did not all have similar kappa numbers, because the empirical pulping model used to calculate the H-factors was not applicable over the entire range of conditions used. Nevertheless, most (90%) were in the range 28±10 and the pulps could

therefore be considered "bleachable." These pulps were used to experimentally obtain preliminary information on the relevant pulping variable effects on bleachability. This was done by subjecting each to a QP bleaching sequence, in which the first stage was an EDTA chelation step and the second was a peroxide delignification stage. The experiment also serves to demonstrate the potential of modern peroxide technology to delignify kraft brownstock, rather than oxygen delignified pulp, the latter application having been thoroughly studied in the course of totally chlorine free sequence development.

## *Experimental*

The pulps were prepared from screened southern pine chips in 500 mL microdigesters. The bombs were equilibrated in a 100°C oil bath, the temperature of which was then increased to maximum cooking temperature over a period of one hour. After washing, screening and kappa number determination, each pulp (10 g. o.d.) was chelated with 0.05% EDTA at pH 6-7 and 10% consistency for one hour at 90°C. It was then washed and bleached with 3% $H_2O_2$ in the presence of 3% NaOH, 0.5% $MgSO_4$ and 0.2% DTPA for 4 hours at 80°C and 10% consistency. Brightness and kappa number were measured by TAPPI test methods.

## *Results and Discussion*

Table 1 represents the central composite rotatable response surface design used and contains the values of the pulping variables used for each cook, together with the corresponding values of the "coded" variables, obtained by applying a coding relationship to the value of the variable expressed in conventional units. For example, the coded temperature, "XT" was obtained by applying the relationship XT = (temperature, °C - 170)/5 and took values ranging from -2 to +2. Using coded values facilitates the analysis and gives regression equations which have coefficients of comparable magnitude.

After bleaching, the brightness gains and kappa number reductions were measured and correlated with the pulping conditions. Table II contains the coded variable levels and the results. It can be seen that the unbleached brightness depended on pulping conditions, varying from 18 to 32. It is also apparent that both the kappa number reductions and the brightness gains were substantial and that they varied as the experimental variables were varied. Degrees of delignification varied from 50 to 70% brightness gains from 27 to 40 points, and final brightnesses from 40 to 69. Because the brightness gain is affected by both chromophore removal and the starting brightness level, the results were also expressed in terms of the change in k/s, the ratio of the absorption coefficient to scattering coefficient. If it can be assumed that the change in scattering coefficient is either small or unaffected by changes in pulping conditions, then changes in k/s decrease will accurately reflect changes in extent of chromophore removal.

The data of Table 2 were subjected to multiple regression analysis to determine which effects were statistically significant and to obtain equations that together serve as a compact summary of the results. Regression analysis of the brightness data, after elimination of one outlying data point (cook 28), gave the following equation:

Unbleached brightness = 27.8 - 0.6 XLW + 1.7 XEA + 0.5 XT - 1.2 XKa

where XKa = (Kappa - 18.5)/5 and for which $R^2$ = 0.95 and residual (error) standard deviation (s) = 0.8. The variables contained in this equation (and the ones below) are the only ones that were statistically significant at the 95% confidence level. The equation shows the known positive effects of decreasing kappa no. and increasing EA charge on unbleached brightness, and also suggests smaller effects due to increasing liquor-to-wood ratio and increasing maximum pulping temperature, the former being detrimental and the latter beneficial. These effects are in need of confirmation, since both are counterintuitive.

Figure 1 shows predicted values calculated from this equation, as lines, together with symbols representing only those data points that were obtained under conditions that correspond to the lines plotted (cooks 1 through 16 of Tables 1 and 2). The distribution of the data points shows that there was considerable undesired correlation between kappa number and the other experimental variables, principally as a result of

inadequacies in the model used to calculate the H-factors. Although the existence of this correlation leaves open the possibility that kappa number is the only important variable, the analysis showed that the other variables were significant at high confidence levels, and it should be kept in mind that the points shown in Figure 1 represent fewer than half of the total number of data points in Table 2. The nature of the experimental design precludes a simple graphical representation of the remaining data points in comparison to their predicted values.

**Table 1. Pulping Conditions and Coded Variable Values for Peroxide Bleachability Study**

| Cook No. | L/W | EA | Sulfidity | Temp | H | Target Kappa | XLW | XEA | XS | XT | XK |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.6 | 15 | 16.3 | 165 | 2875 | 32.5 | -1 | -1 | -1 | -1 | 1 |
| 2 | 7.4 | 15 | 16.3 | 165 | 4550 | 27.5 | 1 | -1 | -1 | -1 | -1 |
| 3 | 4.6 | 21 | 16.3 | 165 | 1900 | 27.5 | -1 | 1 | -1 | -1 | -1 |
| 4 | 7.4 | 21 | 16.3 | 165 | 2690 | 32.5 | 1 | 1 | -1 | -1 | 1 |
| 5 | 4.6 | 15 | 38.8 | 165 | 2050 | 27.5 | -1 | -1 | 1 | -1 | -1 |
| 6 | 7.4 | 15 | 38.8 | 165 | 2560 | 32.5 | 1 | -1 | 1 | -1 | 1 |
| 7 | 4.6 | 21 | 38.8 | 165 | 760 | 32.5 | -1 | 1 | 1 | -1 | 1 |
| 8 | 7.4 | 21 | 38.8 | 165 | 1875 | 27.5 | 1 | 1 | 1 | -1 | -1 |
| 9 | 4.6 | 15 | 16.3 | 175 | 3525 | 27.5 | -1 | -1 | -1 | 1 | -1 |
| 10 | 7.4 | 15 | 16.3 | 175 | 3900 | 32.5 | 1 | -1 | -1 | 1 | 1 |
| 11 | 4.6 | 21 | 16.3 | 175 | 1775 | 32.5 | -1 | 1 | -1 | 1 | 1 |
| 12 | 7.4 | 21 | 16.3 | 175 | 3000 | 27.5 | 1 | 1 | -1 | 1 | -1 |
| 13 | 4.6 | 15 | 38.8 | 175 | 1875 | 32.5 | -1 | -1 | 1 | 1 | 1 |
| 14 | 7.4 | 15 | 38.8 | 175 | 2940 | 27.5 | 1 | -1 | 1 | 1 | -1 |
| 15 | 4.6 | 21 | 38.8 | 175 | 1150 | 27.5 | -1 | 1 | 1 | 1 | -1 |
| 16 | 7.4 | 21 | 38.8 | 175 | 1775 | 32.5 | 1 | 1 | 1 | 1 | 1 |
| 17 | 3.3 | 18 | 27.5 | 170 | 1200 | 30.0 | -2 | 0 | 0 | 0 | 0 |
| 18 | 8.8 | 18 | 27.5 | 170 | 3050 | 30.0 | 2 | 0 | 0 | 0 | 0 |
| 19 | 8.8 | 18 | 27.5 | 170 | 3050 | 30.0 | 2 | 0 | 0 | 0 | 0 |
| 20 | 6.0 | 12 | 27.5 | 170 | 3900 | 30.0 | 0 | -2 | 0 | 0 | 0 |
| 21 | 6.0 | 12 | 27.5 | 170 | 4050 | 30.0 | 0 | -2 | 0 | 0 | 0 |
| 22 | 6.0 | 24 | 27.5 | 170 | 1450 | 30.0 | 0 | 2 | 0 | 0 | 0 |
| 23 | 6.0 | 18 | 5.0 | 170 | 3775 | 30.0 | 0 | 0 | -2 | 0 | 0 |
| 24 | 6.0 | 18 | 40.0 | 170 | 1825 | 30.0 | 0 | 0 | 1.1 | 0 | 0 |
| 25 | 6.0 | 18 | 50.0 | 170 | 2360 | 30.0 | 0 | 0 | 2 | 0 | 0 |
| 26 | 6.0 | 18 | 27.5 | 160 | 2225 | 30.0 | 0 | 0 | 0 | -2 | 0 |
| 27 | 6.0 | 18 | 27.5 | 180 | 2450 | 30.0 | 0 | 0 | 0 | 2 | 0 |
| 28 | 6.0 | 18 | 27.5 | 170 | 2675 | 25.0 | 0 | 0 | 0 | 0 | -2 |
| 29 | 6.0 | 18 | 27.5 | 170 | 2675 | 25.0 | 0 | 0 | 0 | 0 | -2 |
| 30 | 6.0 | 18 | 27.5 | 170 | 2100 | 35.0 | 0 | 0 | 0 | 0 | 2 |
| 31 | 6.0 | 18 | 27.5 | 170 | 2360 | 30.0 | 0 | 0 | 0 | 0 | 0 |
| 32 | 6.0 | 18 | 27.5 | 170 | 2360 | 30.0 | 0 | 0 | 0 | 0 | 0 |
| 33 | 6.0 | 18 | 27.5 | 170 | 2360 | 30.0 | 0 | 0 | 0 | 0 | 0 |
| 34 | 6.0 | 18 | 27.5 | 170 | 2360 | 30.0 | 0 | 0 | 0 | 0 | 0 |
| 35 | 6.0 | 18 | 27.5 | 170 | 2360 | 30.0 | 0 | 0 | 0 | 0 | 0 |
| 36 | 6.0 | 18 | 27.5 | 170 | 2350 | 30.0 | 0 | 0 | 0 | 0 | 0 |
| 37 | 6.0 | 18 | 27.5 | 170 | 2350 | 30.0 | 0 | 0 | 0 | 0 | 0 |
| 38 | 6.0 | 18 | 27.5 | 170 | 2350 | 30.0 | 0 | 0 | 0 | 0 | 0 |

Regression analysis of the absolute decrease in kappa number, after elimination of one outlying data point (cook 28), gave the following equation:

$$\text{Kappa decrease} = 14.8 + 3.7\ XKa + 1.0\ XEA*XKa + 0.6\ XEA^2$$

where XKa = (Kappa - 18.5)/5 and for which $R^2 = 0.97$ and $s = 0.9$. This equation indicates that the reduction in kappa number is greater when the unbleached kappa number is higher, especially for high EA pulps. The predicted dependence on EA is such that increasing EA makes the pulp easier to delignify, except at low unbleached kappa numbers. The equation and the data points are plotted in Figure 2. This figure suggests that the kappa number decrease may be determined only by unbleached kappa number, and that the apparent significance of the other variables is due to the inability of the second-order regression model employed to fit the data with a single curve.

Analysis of the decrease in k/s, was carried out after eliminating five cases identified as outliers by statistical tests. One of these was cook 28, which all other analyses also identified as atypical. Three others,

cooks 13, 31 and 32, were among those that had no measurable residual at the end of the peroxide stage. Cook 23 was eliminated on purely statistical grounds. The following equation was then obtained:

$$k/s \text{ decrease} = 0.860 + 0.045\ XLW - 0.094\ XEA - 0.023\ XT + 0.040\ XKa - 0.024\ XEA*XKa - 0.029\ XT^2$$

for which $R^2 = 0.97$ and $s = 0.038$. The equation indicates that chromophore removal is more extensive at higher unbleached kappa numbers, especially for pulps prepared with low alkali charges. It also indicates a negative effect of high alkali charge, a beneficial effect of high liquor-to-wood ratio, and negative effect of maximum cooking temperature. The equation and the corresponding data points are plotted in Figure 3, which again suggests the possibility that kappa number is the only important variable. Nevertheless the above equation represents a very good fit to the data and the terms other than kappa number are highly significant.

**Table 2. Peroxide Bleaching of Kraft Pulps**

| Cook No. | XLW | XEA | XS | XT | XK | Kappa | Bright-ness | Peroxide Residual, % o.d. pulp | Bleached Kappa | Kappa De-crease | Bleached Bright-ness | Bright-ness Gain | k/s De-crease |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | -1 | -1 | -1 | -1 | 1 | 31.5 | 24.8 | 0.75 | 11.3 | 20.2 | 59.7 | 34.9 | 1.00 |
| 2 | 1 | -1 | -1 | -1 | -1 | 37.9 | 21.6 | 0.04 | 14.2 | 23.7 | 50.5 | 28.9 | 1.18 |
| 3 | -1 | 1 | -1 | -1 | -1 | 22.6 | 30.0 | 0.28 | 7.1 | 15.5 | 65.3 | 35.3 | 0.72 |
| 4 | 1 | 1 | -1 | -1 | 1 | 26.2 | 27.8 | 0.01 | 8.5 | 17.7 | 60.3 | 32.5 | 0.81 |
| 5 | -1 | -1 | 1 | -1 | -1 | 27.7 | 26.2 | 0.01 | 9.5 | 18.2 | 60.5 | 34.3 | 0.91 |
| 6 | 1 | -1 | 1 | -1 | 1 | 34.0 | 24.0 | 0.27 | 11.5 | 22.6 | 60.5 | 36.5 | 1.07 |
| 7 | -1 | 1 | 1 | -1 | 1 | 21.8 | 28.5 | 0.95 | 8.1 | 13.7 | 61.8 | 33.3 | 0.78 |
| 8 | 1 | 1 | 1 | -1 | -1 | 22.3 | 29.0 | 0.43 | 7.7 | 14.6 | 66.0 | 37.0 | 0.78 |
| 9 | -1 | -1 | -1 | 1 | -1 | 27.5 | 26.1 | 0.09 | 8.7 | 18.8 | 61.0 | 34.9 | 0.92 |
| 10 | 1 | -1 | -1 | 1 | 1 | 50.6 | 20.5 | 0.24 | 19.8 | 30.8 | 48.0 | 27.5 | 1.26 |
| 11 | -1 | 1 | -1 | 1 | 1 | 24.1 | 30.7 | 0.66 | 8.1 | 16.0 | 65.9 | 35.2 | 0.69 |
| 12 | 1 | 1 | -1 | 1 | -1 | 24.1 | 29.0 | 0.29 | 7.7 | 16.4 | 65.1 | 36.1 | 0.78 |
| 13 | -1 | -1 | 1 | 1 | 1 | 29.0 | 25.4 | 0.01 | 11.3 | 17.7 | 55.1 | 29.7 | 0.91 |
| 14 | 1 | -1 | 1 | 1 | -1 | 34.0 | 23.0 | 0.33 | 11.6 | 22.4 | 59.2 | 36.2 | 1.15 |
| 15 | -1 | 1 | 1 | 1 | -1 | 21.8 | 31.1 | 0.56 | 8.1 | 13.7 | 67.2 | 36.1 | 0.68 |
| 16 | 1 | 1 | 1 | 1 | 1 | 24.5 | 30.4 | 0.09 | 8.6 | 15.9 | 64.6 | 34.2 | 0.70 |
| 17 | -2 | 0 | 0 | 0 | 0 | 20.6 | 30.5 | 0.57 | 7.4 | 13.2 | 67.6 | 37.1 | 0.71 |
| 18 | 2 | 0 | 0 | 0 | 0 | 29.1 | 24.6 | 0.44 | 10.8 | 18.3 | 60.8 | 36.2 | 1.03 |
| 19 | 2 | 0 | 0 | 0 | 0 | 24.8 | 25.5 | 0.15 | 8.9 | 15.9 | 63.0 | 37.5 | 0.98 |
| 20 | 0 | -2 | 0 | 0 | 0 | 48.3 | 17.7 | 0.02 | 21.3 | 27.0 | 40.9 | 23.2 | 1.49 |
| 21 | 0 | -2 | 0 | 0 | 0 | 44.3 | 18.8 | 0.26 | 21.2 | 23.1 | 45.8 | 27.0 | 1.43 |
| 22 | 0 | 2 | 0 | 0 | 0 | 18.5 | 32.1 | 0.31 | 6.9 | 11.6 | 69.0 | 36.9 | 0.65 |
| 23 | 0 | 0 | -2 | 0 | 0 | 32.7 | 24.8 | 0.19 | 13.1 | 19.6 | 54.6 | 29.8 | 0.95 |
| 24 | 0 | 0 | 1.1 | 0 | 0 | 19.3 | 28.9 | 0.90 | 8.0 | 11.3 | 68.0 | 39.1 | 0.80 |
| 25 | 0 | 0 | 2 | 0 | 0 | 24.2 | 27.3 | 0.10 | 9.4 | 14.8 | 65.2 | 37.9 | 0.88 |
| 26 | 0 | 0 | 0 | -2 | 0 | 22.0 | 27.2 | 0.01 | 10.5 | 11.5 | 55.7 | 28.5 | 0.80 |
| 27 | 0 | 0 | 0 | 2 | 0 | 19.8 | 30.7 | 0.01 | 9.1 | 10.7 | 60.0 | 29.3 | 0.65 |
| 28 | 0 | 0 | 0 | 0 | -2 | 25.1 | 24.3 | 0.97 | 9.8 | 15.3 | 63.6 | 39.3 | 1.07 |
| 29 | 0 | 0 | 0 | 0 | -2 | 20.0 | 28.0 | 0.07 | 7.2 | 12.8 | 62.2 | 34.2 | 0.81 |
| 30 | 0 | 0 | 0 | 0 | 2 | 22.8 | 28.3 | 0.43 | 8.0 | 14.8 | 65.9 | 37.6 | 0.82 |
| 31 | 0 | 0 | 0 | 0 | 0 | 20.3 | 30.4 | 0.19 | 8.1 | 12.2 | 63.9 | 33.5 | 0.69 |
| 32 | 0 | 0 | 0 | 0 | 0 | 19.6 | 29.0 | 0.01 | 7.7 | 11.9 | 61.1 | 32.1 | 0.75 |
| 33 | 0 | 0 | 0 | 0 | 0 | 19.8 | 28.1 | 0.25 | 8.0 | 11.8 | 64.6 | 36.5 | 0.82 |
| 34 | 0 | 0 | 0 | 0 | 0 | 21.6 | 28.3 | 0.60 | 8.3 | 13.3 | 66.2 | 37.9 | 0.82 |
| 35 | 0 | 0 | 0 | 0 | 0 | 21.9 | 27.5 | 0.58 | 8.0 | 13.9 | 66.8 | 39.3 | 0.87 |
| 36 | 0 | 0 | 0 | 0 | 0 | 20.1 | 26.8 | 0.54 | 8.5 | 11.6 | 66.8 | 40.0 | 0.92 |
| 37 | 0 | 0 | 0 | 0 | 0 | 19.3 | 28.9 | 0.25 | 6.8 | 12.5 | 68.0 | 39.1 | 0.80 |
| 38 | 0 | 0 | 0 | 0 | 0 | 19.4 | 28.2 | 0.22 | 7.2 | 12.2 | 66.6 | 38.4 | 0.83 |

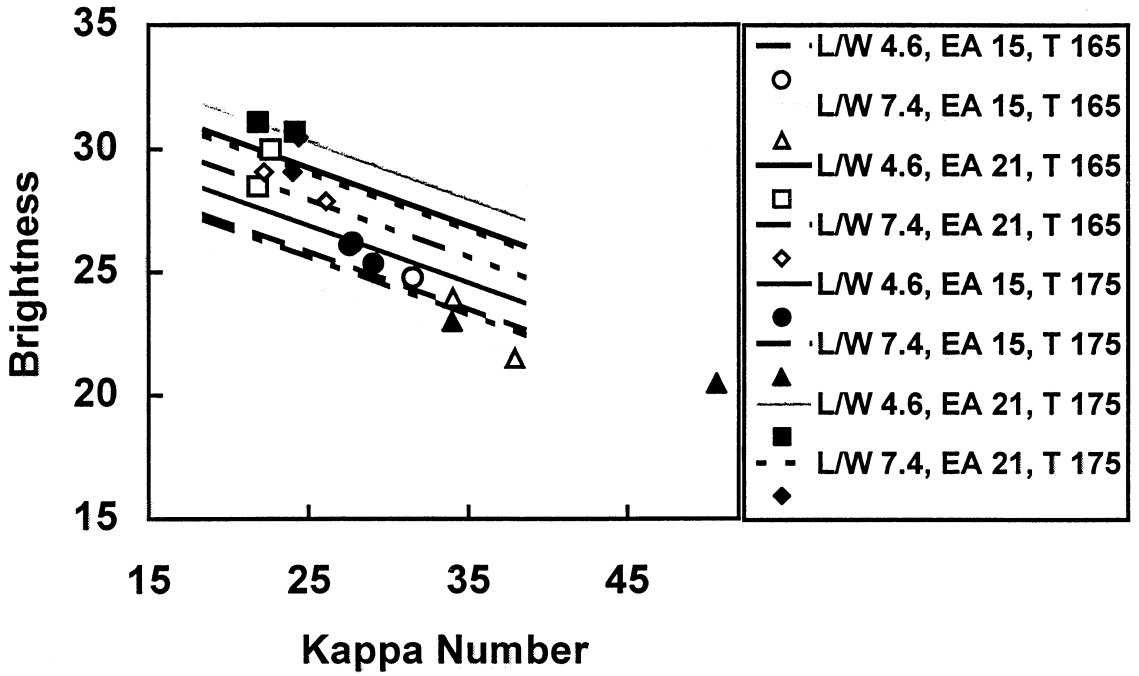


**Figure 1. Predicted and corresponding observed values of unbleached pulp brightness.**

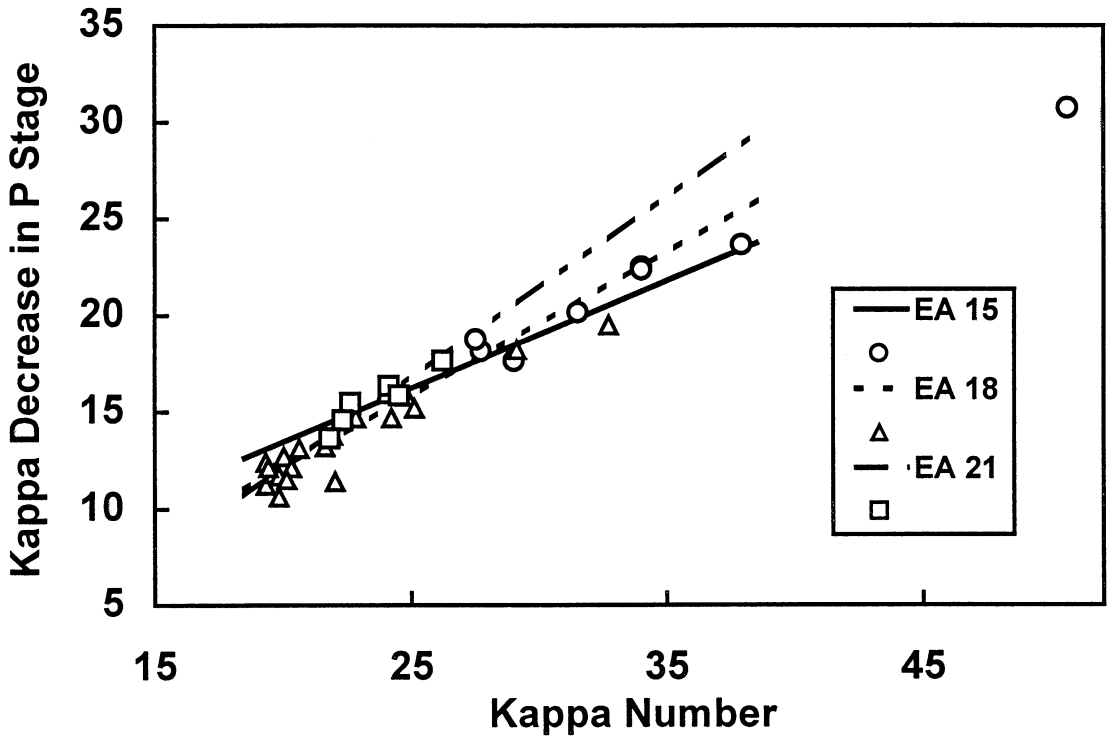


**Figure 2. Kappa number decrease predicted by regression equation (lines) and observed (symbols).**

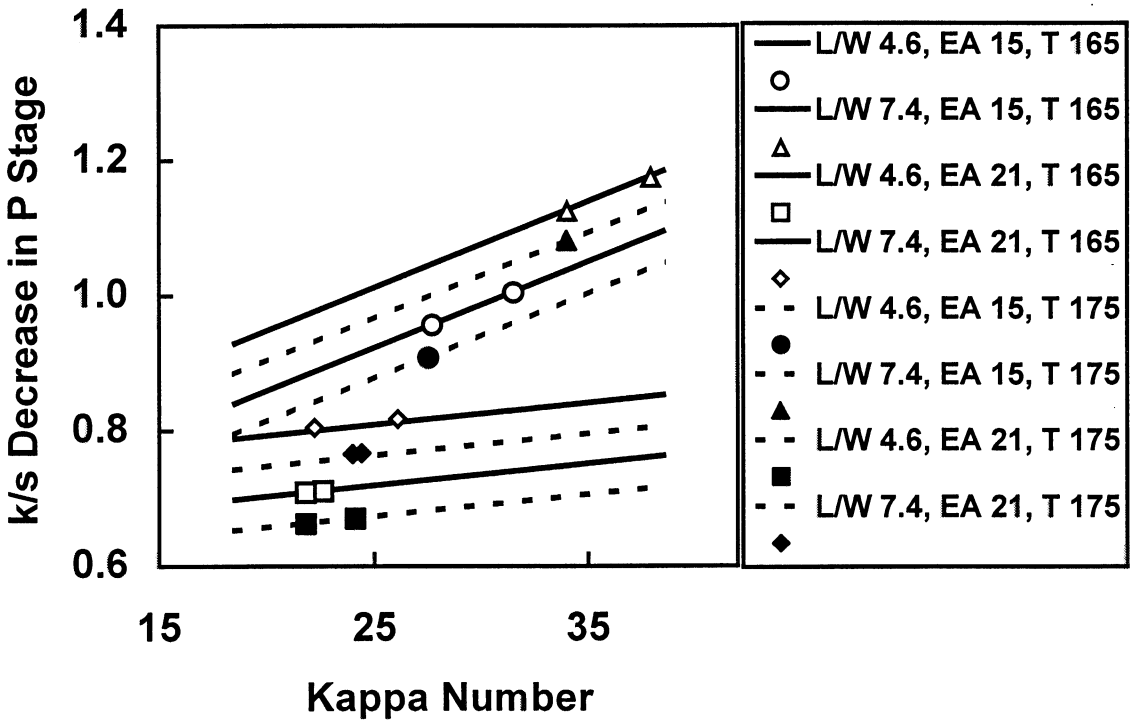


**Figure 3. k/s decrease predicted by regression equation (lines) and observed (symbols).**

### *Summary and Conclusions*

Modern chelation-peroxide technology is capable of extensively delignifying southern pine kraft brownstock produced under a wide variety of pulping conditions and over wide range of kappa numbers. The unbleached brightness of the pulps increases with decreasing kappa number and increasing EA charge, and may also be positively affected by increased cooking temperature and negatively affected by increased liquor-to-wood ratio. The decrease in kappa number upon chelation followed by peroxide treatment increases with increasing unbleached kappa number. The corresponding decrease in chromophore content, as measured by the observed decrease in k/s, is higher for high kappa number pulps, especially when those pulps were produced with a low EA charge. There may also be a negative effect of high alkali charge, a beneficial effect of high liquor-to-wood ratio, and negative effect of maximum cooking temperature.

## Comparison of Effects of Carryover and $D_1$ Stage pH in ECF and (DC)-Based Bleaching

### *Introduction*

Bleaching sequences based on the use of $ClO_2$ as the only delignifying agent (ECF sequences) are becoming widespread and will be almost universally adopted within a very few years when the Cluster Rule takes full effect. Although some mills have already been practicing ECF bleaching for some time, the experience base is nevertheless much more narrow than in the case of chlorine-based or intermediate substitution sequences. It is probable that there is still much to be learned about ECF process behavior and that there is a corresponding opportunity to improve the efficiency of the process. Accordingly, we undertook a comparative study of short ECF and 50% substitution sequences to learn whether there are differences in their behaviors with respect to kappa factor (KF) and $D_1$ stage pH. One of the objectives of

this study was to perform the evaluation under realistic conditions of brown stock washing and stage-to-stage carryover, instead of resorting to the usual lab practice of perfect washing between stages. At the same time, we wished to evaluate the sensitivity of both processes to washing inefficiency, so the perfectly washed case was included as a control.

The experiment was planned as a full factorial arrangement with two levels of $ClO_2$ substitution (50 and 100%), two levels of KF (0.15 and 0.25), two levels of carryover (none and a set of standard levels), and three levels of $D_1$ pH (3, 4, and 5). In fact, more than three levels of $D_1$ pH were investigated at most combinations of levels of the other variables, because of the difficulty in consistently predicting exit pH under the variety of conditions used. The unbleached pulp was a single batch prepared in the laboratory from southern pine chips. The pulp, after screening, was enriched in shives, to make differences in dirt bleaching easier to see.

## *Experimental*

### Pulping

Three 6000 g o.d. batches of southern pine chips were cooked in an externally heated digester to an H-factor of 1650 at a maximum temperature of 170 °C, a liquor-to-wood ratio of 4.0, an EA charge of 16% and 25% sulfidity. The three pulps were screened, washed, blended and dewatered to give a single large batch of pulp having a kappa number of 30.3. The kappa numbers before blending were 28.1, 31.6 and 32.3. The black liquors were combined, tested to determine that the solids content was 13%, and stored cold for use in the bleaching experiments. Shives were obtained by making two additional cooks to kappa number 46 and refining and screening the resulting pulps. The shives obtained were added to the bleachable pulp at the rate of 3.54 g per 100 g pulp.

### Bleaching

A 200 g o.d. sample of unbleached pulp (including added shives) was preheated and placed in a well-mixed 20L cylindrical reactor. The pH of the pulp was adjusted to approximately 2.5 before being introduced into the reactor. Bleaching was conducted for 30 min. at 45 °C and 2% consistency. For (DC) stages, the $Cl_2$was added 30 sec. After the $ClO_2$. After bleaching the filtrate was collected before washing the pulp and stored for use in later bleaching stages. The pulp was thoroughly washed by repeated dilution to 3% consistency and thickening. The washed pulp was mixed with the amount of NaOH required for the (EO) stage, together with dilution water and $D_0$ stage carryover when required. It was then placed in a stainless steel reactor equipped with a horizontal-shaft pin mixer and subjected to an (EO) stage under the following conditions: 60 min., 70°C, 10 % consistency, %NaOH = 0.65*TAC at 0.15 KF or 0.45*TAC at 0.25 KF, $O_2$ pressure initially 60 psig., decreasing by 10 psig every 5 minutes. The $D_1$ stage was conducted at 10% consistency and 70°C for a maximum of 180 minutes, being terminated after a shorter time if it became obvious that the residual was exhausted or nearly exhausted. Carryover, when used, was applied at the following levels: black liquor solids into the $D_0$ or (DC) stage corresponding to a brown stock washing efficiency of 95.2% (1% of the liquid in the $D_0$ or (DC) stage); $D_0$ or (DC) filtrate equivalent to 10% of the liquid in the (EO) stage; and (EO) filtrate to the $D_1$ stage amounting to 20% of the liquid in the $D_1$ stage.

## *Results and Discussion*

Tables 3 through 6 contain the experimental data for the four different combinations of substitution and KF. The low brightnesses obtained when carryover was used should be viewed in light of the fact that a substantial amount of black liquor was added, to exaggerate the effect and detect smaller differences. In the absence of carryover, a brightness value of 80 or higher was achieved, even at the low KF.

Table 3. $D_0(EO)D_1$ Bleaching at 0.15 Kappa Factor

| | (EO) Stage | | | | | | | $D_1$ Stage | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Carry-over | (EO) Kappa No. | Bright-ness | Reverted Brightness | Loss | PC No. | Dirt, ppm | Visc., mPa.s | $ClO_2$, % o.d. pulp | Initial pH | Final pH | Time, Min. | Resid. $ClO_2$, % o.d. pulp | Bright-ness | Reverted Brightness | Loss | PC No. | Dirt, ppm | Visc., mPa.s |
| 0 | 7.9 | 48.7 | 45.2 | 3.5 | 6.2 | 50 | 24.7 | 0.4 | 2.75 | 2.47 | 180 | 0.000 | 59.5 | 54.1 | 5.4 | 5.7 | | |
| | | | | | | | | | 3.80 | 2.85 | 180 | 0.000 | 60.4 | 54.7 | 5.7 | 5.8 | 113 | 19.1 |
| | | | | | | | | | 5.85 | 4.48 | 180 | 0.000 | 66.0 | 60.0 | 6.0 | 4.6 | 82 | 22.7 |
| | | | | | | | | | 6.42 | 4.73 | 180 | 0.000 | 67.1 | 59.5 | 7.6 | 5.7 | | 22.6 |
| | | | | | | | | | 6.50 | 5.16 | 180 | 0.014 | 67.5 | 60.4 | 7.1 | 5.2 | 63 | 23.4 |
| | | | | | | | | | 6.97 | 5.85 | 180 | 0.049 | 67.2 | 60.4 | 6.8 | 5.0 | 128 | 22.7 |
| 1 | 16.4 | 38.6 | 36.8 | 1.8 | 5.4 | 49 | 26.3 | 0.4 | 2.40 | 2.30 | 165 | 0.000 | 36.2 | 33.1 | 3.1 | 11.4 | 69 | 21.9 |
| | | | | | | | | | 2.65 | 2.65 | 125 | 0.000 | 36.8 | 33.9 | 2.9 | 10.2 | 49 | 21.9 |
| | | | | | | | | | 3.65 | 3.75 | 165 | 0.000 | 39.3 | 36.2 | 3.1 | 9.3 | 55 | 23.1 |
| | | | | | | | | | 5.05 | 4.55 | 115 | 0.000 | 39.9 | 37.2 | 2.7 | 7.7 | | 28.3 |
| | | | | | | | | | 6.00 | 5.65 | 165 | 0.001 | 39.8 | 37.7 | 2.1 | 5.9 | | 26.0 |
| 0 | 7.2 | 50.6 | 47.1 | 3.5 | 5.6 | | 26.0 | 0.8 | 3.45 | 2.15 | 180 | 0.000 | 69.0 | 62.1 | 6.9 | 4.6 | 90 | 22.0 |
| | | | | | | | | | 6.35 | 3.10 | 180 | 0.000 | 70.4 | 63.8 | 6.6 | 4.0 | 95 | 20.5 |
| | | | | | | | | | 7.00 | 4.02 | 180 | 0.000 | 72.6 | 66.4 | 6.2 | 3.3 | | 25.5 |
| | | | | | | | | | 7.30 | 4.38 | 180 | 0.000 | 74.8 | 67.5 | 7.3 | 3.6 | 55 | 23.7 |
| | | | | | | | | | 7.60 | 4.96 | 180 | 0.083 | 76.8 | 68.6 | 8.2 | 3.7 | | 24.0 |
| | | | | | | | | | 8.00 | 5.76 | 180 | 0.175 | 74.6 | 66.5 | 8.1 | 4.1 | 87 | 23.1 |
| 1 | 15.7 | 39.3 | 37.1 | 2.2 | 6.4 | | 28.1 | 0.8 | 3.15 | 2.80 | 100 | 0.000 | 39.0 | 35.3 | 3.7 | 11.6 | 30 | 23.0 |
| | | | | | | | | | 4.15 | 3.60 | 115 | 0.000 | 42.7 | 38.1 | 4.6 | 11.8 | 38 | 25.1 |
| | | | | | | | | | 5.60 | 4.65 | 120 | 0.000 | 46.1 | 41.4 | 4.7 | 10.0 | 64 | 26.2 |
| | | | | | | | | | 6.20 | 4.95 | 115 | 0.001 | 45.5 | 41.7 | 3.8 | 8.1 | | 27.1 |
| | | | | | | | | | 7.00 | 6.20 | 120 | 0.103 | 43.6 | 40.0 | 3.6 | 8.5 | | 22.9 |
| 0 | 7.91 | 48.6 | 45 | 3.6 | 6.4 | | 26.0 | 1.6 | 3.30 | 1.70 | 160 | 0.000 | 77.1 | 67.4 | 9.7 | 4.5 | 87 | 20.7 |
| | | | | | | | | | 6.60 | 2.35 | 165 | 0.000 | 78.1 | 69.0 | 9.1 | 3.9 | 101 | 21.1 |
| | | | | | | | | | 7.55 | 3.25 | 155 | 0.000 | 80.2 | 71.6 | 8.6 | 3.2 | 81 | 20.7 |
| | | | | | | | | | 8.40 | 4.15 | 85 | 0.005 | 80.9 | 72.7 | 8.2 | 2.9 | 62 | 23.9 |
| 1 | 16.44 | 38.5 | 36.6 | 1.9 | 5.8 | | 27.1 | 1.6 | 3.50 | 2.35 | 115 | 0.000 | 45.5 | 40.0 | 5.5 | 12.4 | 60 | 24.0 |
| | | | | | | | | | 4.95 | 2.70 | 125 | 0.000 | 47.2 | 41.4 | 5.8 | 11.9 | 68 | |
| | | | | | | | | | 6.40 | 4.20 | 120 | 0.000 | 54.8 | 47.7 | 7.1 | 10.0 | 86 | 26.2 |
| | | | | | | | | | 6.60 | 4.70 | 110 | 0.044 | 57.0 | 49.9 | 7.1 | 8.9 | 76 | 27.6 |
| | | | | | | | | | 6.85 | 5.15 | 125 | 0.131 | 55.6 | 48.7 | 6.9 | 9.3 | 67 | 29.3 |

Table 4. $D_0(EO)D_1$ Bleaching at 0.25 Kappa Factor

| | (EO) Stage | | | | | | | $D_1$ Stage | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Carry-over | (EO) Kappa No. | Bright-ness | Reverted Brightness | Loss | PC No. | Dirt | Visc., mPa.s | $ClO_2$, % o.d. pulp | Initial pH | Final pH | Time, Min. | Resid. $ClO_2$, % o.d. pulp | Bright-ness | Reverted Brightness | Loss | PC No. | Dirt | Visc., mPa.s |
| 0 | 5.01 | 55.8 | 51.7 | 4.1 | 5.1 | 65.8 | 25.7 | 0.4 | 2.45 | 2.19 | 180 | 0.000 | 69.5 | 63.2 | 6.3 | 4.0 | 26 | 21.0 |
| | | | | | | | | | 4.15 | 2.85 | 180 | 0.000 | 70.5 | 64.1 | 6.4 | 3.9 | 29 | 22.1 |
| | | | | | | | | | 4.42 | 3.01 | 155 | 0.000 | 71.2 | 64.3 | 6.9 | 4.1 | | 22.5 |
| | | | | | | | | | 5.70 | 3.45 | 150 | 0.000 | 71.9 | 65.3 | 6.6 | 3.7 | | 23.2 |
| | | | | | | | | | 5.70 | 3.61 | 180 | 0.000 | 72.1 | 65.8 | 6.3 | 3.5 | 50 | 23.9 |
| | | | | | | | | | 6.83 | 5.04 | 180 | 0.058 | 76.0 | 68.2 | 7.8 | 3.6 | 63 | 25.0 |
| 1 | 8.66 | 47.3 | 44.2 | 3.1 | 5.9 | 64.8 | 26.4 | 0.4 | 2.30 | 2.25 | 120 | 0.000 | 50.1 | 45.6 | 4.5 | 7.6 | 59 | 22.5 |
| | | | | | | | | | 4.50 | 4.20 | 120 | 0.000 | 54.4 | 49.7 | 4.7 | 6.3 | 46 | 24.5 |
| | | | | | | | | | 5.50 | 5.10 | 125 | 0.001 | 54.7 | 49.5 | 5.2 | 7.0 | 54 | 25.8 |
| | | | | | | | | | 6.30 | 5.95 | 120 | 0.029 | 53.8 | 49.2 | 4.6 | 6.4 | 57 | 26.7 |
| 0 | 4.96 | 55.3 | 51 | 4.3 | 5.5 | | 26.3 | 0.8 | 3.10 | 2.12 | 180 | 0.000 | 78.2 | 70.0 | 8.2 | 3.4 | 48 | 21.5 |
| | | | | | | | | | 6.53 | 2.82 | 180 | 0.000 | 79.7 | 72.2 | 7.5 | 2.8 | 59 | 22.3 |
| | | | | | | | | | 6.95 | 3.70 | 105 | 0.000 | 81.9 | 74.1 | 7.8 | 2.5 | | 23.7 |
| | | | | | | | | | 7.30 | 3.82 | 180 | 0.000 | 81.8 | 74.6 | 7.2 | 2.3 | 54 | 24.7 |
| | | | | | | | | | 7.70 | 4.82 | 180 | 0.000 | 82.7 | 74.9 | 7.8 | 2.4 | | 24.6 |
| 1 | 9.18 | 46.7 | 43.4 | 3.3 | 6.5 | | 23.2 | 0.8 | 2.70 | 2.30 | 125 | 0.000 | 55.0 | 49.9 | 5.1 | 6.7 | 54 | 23.6 |
| | | | | | | | | | 4.40 | 3.15 | 120 | 0.000 | 56.9 | 51.0 | 5.9 | 7.2 | 66 | 25.1 |
| | | | | | | | | | 6.30 | 4.60 | 125 | 0.001 | 64.0 | 57.3 | 6.7 | 5.8 | 82 | 26.6 |
| | | | | | | | | | 6.90 | 5.80 | 115 | 0.117 | 62.3 | 55.4 | 6.9 | 6.5 | 63 | 25.8 |
| 0 | 4.89 | 57.9 | 53.7 | 4.2 | 4.7 | | 27.3 | 1.6 | 5.40 | 2.35 | 180 | 0.053 | 84.1 | 76.2 | 7.9 | 2.2 | 106 | 21.1 |
| | | | | | | | | | 8.00 | 3.20 | 180 | 0.01. | 86.0 | 79.5 | 6.5 | 1.5 | 111 | 23.6 |
| | | | | | | | | | 10.25 | 4.15 | 150 | 0.073 | 85.9 | 79.4 | 6.5 | 1.5 | 94 | 20.5 |
| | | | | | | | | | 10.45 | 4.60 | 170 | 0.073 | 85.6 | 79.4 | 6.2 | 1.5 | | |
| | | | | | | | | | 10.50 | 4.75 | 110 | 0.185 | 84.8 | 77.6 | 7.2 | 1.9 | 102 | 18.6 |
| 1 | 10.03 | 46.4 | 43.4 | 3.0 | 5.9 | | 28.8 | 1.6 | 2.75 | 2.05 | 115 | 0.000 | 62.9 | 55.8 | 7.1 | 6.6 | 45 | 23.7 |
| | | | | | | | | | 6.35 | 3.00 | 145 | 0.000 | 65.8 | 59.0 | 6.8 | 5.4 | 87 | 26.9 |
| | | | | | | | | | 6.85 | 3.70 | 120 | 0.000 | 67.1 | 60.6 | 6.5 | 4.7 | 69 | |
| | | | | | | | | | 7.30 | 4.70 | 130 | 0.034 | 73.6 | 63.5 | 10.1 | 5.8 | 73 | 26.8 |
| | | | | | | | | | 7.20 | 4.70 | 130 | 0.083 | 74.1 | 65.6 | 8.5 | 4.5 | | |
| | | | | | | | | | 9.00 | 6.50 | 115 | 0.462 | 66.8 | 59.5 | 7.3 | 5.5 | | 25.2 |

Table 5. (DC)(EO)$D_1$ Bleaching at 0.15 Kappa Factor

| | (EO) Stage | | | | | | | $D_1$ Stage | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Carry-over | (EO) Kappa No. | Bright-ness | Reverted Brightness | Loss | PC No. | Dirt | Visc., mPa.s | $ClO_2$, % o.d. pulp | Initial pH | Final pH | Time, Min. | Resid. $ClO_2$, % o.d. pulp | Bright-ness | Reverted Brightness | Loss | PC No. | Dirt | Visc., mPa.s |
| 0 | 7.78 | 44.9 | 42.2 | 2.7 | 5.7 | 40.0 | 26.4 | 0.4 | 2.45 | 2.20 | 135 | 0.000 | 50.8 | 45.6 | 5.2 | 8.6 | 38 | |
| | | | | | | | | | 4.05 | 3.15 | 125 | 0.000 | 53.5 | 48.1 | 5.4 | 7.8 | 64 | |
| | | | | | | | | | 5.50 | 4.30 | 120 | 0.000 | 56.9 | 51.1 | 5.8 | 7.1 | 57 | 23.1 |
| | | | | | | | | | 6.50 | 5.40 | 145 | 0.029 | 55.1 | 49.9 | 5.2 | 6.9 | 60 | |
| 1 | 16.97 | 36.2 | 34.4 | 1.7 | 6.0 | 45.0 | 27.3 | 0.4 | 2.25 | 2.20 | 125 | 0.000 | 33.5 | 31.1 | 2.4 | 10.3 | 27 | |
| | | | | | | | | | 3.80 | 3.40 | 125 | 0.000 | 34.8 | 32.5 | 2.3 | 9.0 | 50 | |
| | | | | | | | | | 5.25 | 4.65 | 135 | 0.000 | 38.0 | 35.2 | 2.8 | 9.1 | 38 | |
| | | | | | | | | | 5.80 | 5.20 | 120 | 0.000 | 37.2 | 35.0 | 2.2 | 7.3 | | |
| | | | | | | | | | 6.70 | 6.10 | 125 | 0.010 | 38.2 | 36.0 | 2.2 | 6.9 | 46 | 29.6 |
| 0 | 7.93 | 44.8 | 42.1 | 2.7 | 5.8 | | 28.6 | 0.8 | 2.55 | 2.20 | 135 | 0.000 | 59.6 | 53.3 | 6.3 | 6.8 | 51 | |
| | | | | | | | | | 5.55 | 2.85 | 145 | 0.000 | 62.3 | 56.0 | 6.3 | 5.9 | 51 | |
| | | | | | | | | | 6.70 | 4.10 | 150 | 0.000 | 69.0 | 60.9 | 8.1 | 5.6 | 101 | 24.6 |
| | | | | | | | | | 6.45 | 3.84 | 110 | 0.000 | 68.7 | 61.1 | 7.6 | 5.3 | | |
| | | | | | | | | | 6.90 | 4.45 | 120 | 0.078 | 68.2 | 60.2 | 8.0 | 5.7 | | |
| | | | | | | | | | 7.05 | 5.15 | 150 | 0.122 | 67.5 | 59.9 | 7.6 | 5.6 | 72 | |
| 1 | 18.55 | 35.8 | 34.2 | 1.6 | 5.7 | | 28.1 | 0.8 | 2.55 | 2.45 | 125 | 0.000 | 31.4 | 28.9 | 2.5 | 12.5 | 29 | |
| | | | | | | | | | 2.55 | 2.45 | 125 | 0.000 | 32.5 | 29.4 | 3.1 | 14.7 | | |
| | | | | | | | | | 4.05 | 3.20 | 125 | 0.000 | 35.0 | 32.2 | 2.8 | 11.0 | 37 | 24.1 |
| | | | | | | | | | 5.80 | 4.60 | 140 | 0.000 | 39.8 | 36.6 | 3.2 | 9.4 | 37 | |
| | | | | | | | | | 6.55 | 5.30 | 120 | 0.001 | 40.4 | 37.1 | 3.3 | 9.4 | 39 | |
| | | | | | | | | | 6.86 | 5.72 | 120 | 0.034 | 38.9 | 36.3 | 2.6 | 7.9 | | |
| 0 | 8.15 | 44.9 | 42.3 | 2.6 | 5.5 | | 27.4 | 1.6 | 4.05 | 1.80 | 180 | 0.000 | 73.4 | 64.7 | 8.7 | 4.8 | 55 | |
| | | | | | | | | | 6.80 | 2.50 | 180 | 0.000 | 76.1 | 68.1 | 8.0 | 3.7 | 60 | |
| | | | | | | | | | 7.30 | 3.20 | 180 | 0.000 | 77.3 | 69.2 | 8.1 | 3.5 | 52 | |
| | | | | | | | | | 7.85 | 3.80 | 120 | 0.000 | 80.2 | 72.2 | 8.0 | 2.9 | | |
| | | | | | | | | | 8.30 | 4.20 | 160 | 0.019 | 80.2 | 71.9 | 8.3 | 3.0 | 55 | 23.8 |
| | | | | | | | | | 9.10 | 6.10 | 130 | 0.500 | 73.1 | 65.5 | 7.6 | 4.1 | | |
| 1 | 18.52 | 36.1 | 34.6 | 1.5 | 5.3 | | 27.4 | 1.6 | 2.90 | 2.15 | 150 | 0.000 | 37.9 | 34.2 | 3.7 | 12.4 | 39 | |
| | | | | | | | | | 5.45 | 3.30 | 140 | 0.000 | 42.0 | 37.9 | 4.1 | 10.8 | 56 | |
| | | | | | | | | | 6.35 | 4.15 | 130 | 0.000 | 49.6 | 43.7 | 5.9 | 10.7 | 43 | 25.5 |
| | | | | | | | | | 6.60 | 4.65 | 130 | 0.034 | 51.9 | 46.3 | 5.6 | 8.9 | | 27.5 |
| | | | | | | | | | 6.75 | 5.30 | 125 | 0.102 | 49.6 | 44.0 | 5.6 | 10.0 | 58 | |

Table 6. (DC)(EO)$D_1$ Bleaching at 0.25 Kappa Factor

| | (EO) Stage | | | | | | | $D_1$ Stage | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Carry-over | (EO) Kappa No. | Bright-ness | Reverted Brightness | Loss | PC No. | Dirt | Visc., mPa.s | ClO2, % o.d. pulp | Initial pH | Final pH | Time, Min. | Resid. ClO2, % o.d. pulp | Bright-ness | Reverted Brightness | Loss | PC No. | Dirt | Visc., mPa.s |
| 0 | 3.41 | 53.1 | 49.5 | 3.6 | 5.0 | 58.0 | 25.9 | 0.4 | 2.50 | 2.10 | 110 | 0.000 | 72.8 | 65.0 | 7.8 | 4.3 | 59 | |
| | | | | | | | | | 3.90 | 2.60 | 115 | 0.000 | 72.0 | 64.4 | 7.6 | 4.4 | 81 | |
| | | | | | | | | | 5.70 | 3.25 | 150 | 0.000 | 75.3 | 67.7 | 7.6 | 3.7 | 63 | |
| | | | | | | | | | 6.45 | 4.05 | 160 | 0.005 | 78.2 | 70.5 | 7.7 | 3.1 | 91 | 20.8 |
| | | | | | | | | | 7.75 | 5.20 | 120 | 0.090 | 77.4 | 69.5 | 7.9 | 3.4 | | |
| | | | | | | | | | 8.75 | 6.87 | 120 | 0.146 | 73.5 | 66.7 | 6.8 | 3.5 | | |
| 1 | 13.1 | 39.0 | 36.9 | 2.1 | 6.2 | 35.0 | 25.2 | 0.4 | 2.60 | 2.60 | 155 | 0.000 | 36.4 | 34.0 | 2.4 | 8.5 | 37 | |
| | | | | | | | | | 4.45 | 3.90 | 120 | 0.001 | 40.9 | 38.1 | 2.8 | 7.6 | 55 | |
| | | | | | | | | | 5.30 | 4.55 | 105 | 0.000 | 40.8 | 38.1 | 2.7 | 7.3 | | |
| | | | | | | | | | 5.45 | 4.65 | 115 | 0.000 | 40.1 | 37.6 | 2.5 | 7.0 | | |
| | | | | | | | | | 6.35 | 5.60 | 130 | 0.000 | 40.9 | 38.2 | 2.7 | 7.3 | 45 | 27.9 |
| 0 | 2.6 | 59.0 | 55.0 | 4.0 | 4.2 | | 23.4 | 0.8 | 2.65 | 2.35 | 150 | 0.019 | 85.5 | 76.9 | 8.6 | 2.2 | 51 | |
| | | | | | | | | | 7.35 | 3.30 | 150 | 0.007 | 87.1 | 80.7 | 6.4 | 1.4 | 78 | |
| | | | | | | | | | 10.30 | 4.50 | 180 | 0.068 | 87.1 | 81.4 | 5.7 | 1.2 | 111 | 20.3 |
| | | | | | | | | | 10.30 | 4.50 | 180 | 0.058 | 87.4 | 81.1 | 6.3 | 1.3 | | |
| | | | | | | | | | 11.00 | 6.50 | 180 | 0.253 | 82.7 | 77.1 | 5.6 | 1.6 | 95 | |
| 1 | 12.05 | 40.8 | 38.7 | 2.1 | 5.6 | | 25.5 | 0.8 | 2.40 | 2.35 | 110 | 0.000 | 41.9 | 37.7 | 4.2 | 11.2 | 41 | |
| | | | | | | | | | 3.45 | 2.85 | 115 | 0.000 | 41.8 | 38.2 | 3.6 | 9.5 | | |
| | | | | | | | | | 4.65 | 3.70 | 135 | 0.000 | 45.7 | 41.7 | 4.0 | 8.5 | 56 | 24.6 |
| | | | | | | | | | 4.95 | 3.90 | 115 | 0.000 | 47.9 | 43.6 | 4.3 | 8.1 | | 25.9 |
| | | | | | | | | | 6.00 | 4.90 | 110 | 0.001 | 50.8 | 45.8 | 5.0 | 8.2 | 84 | |
| | | | | | | | | | 6.60 | 5.50 | 135 | 0.022 | 49.2 | 45.2 | 4.0 | 7.0 | 42 | |
| 0 | 2.78 | 57.4 | 53.5 | 3.9 | 4.4 | | 24.5 | 1.6 | 4.80 | 2.15 | 180 | 0.126 | 86.9 | 78.8 | 8.1 | 1.9 | 39 | |
| | | | | | | | | | 6.30 | 2.60 | 175 | 0.073 | 88.0 | 81.9 | 6.1 | 1.2 | | |
| | | | | | | | | | 8.80 | 3.70 | 175 | 0.097 | 88.7 | 82.4 | 6.3 | 1.2 | 43 | 22.4 |
| | | | | | | | | | 10.45 | 4.20 | 180 | 0.112 | 88.4 | 81.7 | 6.7 | 1.3 | 52 | 20.3 |
| | | | | | | | | | 10.70 | 4.65 | 105 | 0.151 | 88.2 | 82.0 | 6.2 | 1.2 | | |
| | | | | | | | | | 11.25 | 5.80 | 170 | 0.350 | 87.2 | 79.7 | 7.5 | 1.6 | 65 | |
| 1 | 11.45 | 40.3 | 37.9 | 2.4 | 6.7 | | 26.7 | 1.6 | 2.50 | 2.00 | 110 | 0.000 | 52.5 | 46.2 | 6.3 | 9.8 | 35 | |
| | | | | | | | | | 5.85 | 2.90 | 120 | 0.000 | 54.8 | 48.6 | 6.2 | 8.5 | | |
| | | | | | | | | | 6.30 | 3.60 | 105 | 0.000 | 58.6 | 51.6 | 7.0 | 8.1 | | |
| | | | | | | | | | 6.70 | 4.35 | 125 | 0.029 | 65.0 | 57.0 | 8.0 | 6.8 | | 24.0 |
| | | | | | | | | | 6.80 | 4.70 | 135 | 0.078 | 65.9 | 58.6 | 7.3 | 5.8 | | |
| | | | | | | | | | 6.90 | 5.60 | 130 | 0.209 | 61.4 | 54.7 | 6.7 | 6.6 | | |

Analysis of the data of Tables 3 through 6 is in progress at the time of writing. Analysis of variance of the (EO) kappa number data showed that all three variables had significant effects and that all interacted significantly with one another. Figure 4 shows the relevant relationships. As expected, carryover increased the (EO) kappa number under all conditions of substitution and KF. At low KF, carryover had about the same effect on $D_0$ and (DC) bleaching. However, at high KF, carryover had significantly less effect on The $D_0$ stage than on the (DC) stage. It is hypothesized that this is due to the presence in the dissolved organic black liquor solids of a fraction which is unreactive toward $ClO_2$ but reactive toward $Cl_2$. The reactive fraction is consumed at low KF and when the KF is increased the fraction that remains consumes less $ClO_2$ than $Cl_2$. The practical implication is that the $D_0$ stage may be expected to be less affected by poor brown stock washing than the (DC) stage.

All of the bleached brightness data were simultaneously subjected to multiple regression analysis to determine which effects are significant and to summarize the data in compact form. A second order model was tried initially and a poor fit was obtained. This was apparent from a comparison of the data at a given combination of the first three variables with the predicted $D_1$ pH - brightness relationships. It was also apparent from a disparity between the residual standard deviation and the scatter of the points around curves manually fit to the $D_1$ pH - brightness data at each combination of the first three variables. A third-order model was then tried, and a considerably improved fit was obtained. This model is shown, together with the brightness data, in Figures 4 through 7. It can be seen that the fit is still not as good as it might be, but it serves to illustrate the main trends and establishes their statistical significance. Further attempts will be made to improve the model by making selected fourth-order terms available. This may uncover additional significant features of the data, but is unlikely to change the conclusions regarding those already identified.

A few general observations that can be made even before completing the data analysis are that final brightness is higher for $D_0$ than for (DC) when carryover is high, and that the optimum $D_1$ exit pH is higher at low KF than at high KF and higher in the presence of carryover than in its absence, both of these effects being greater for ECF than for bleaching at the lower substitution level.

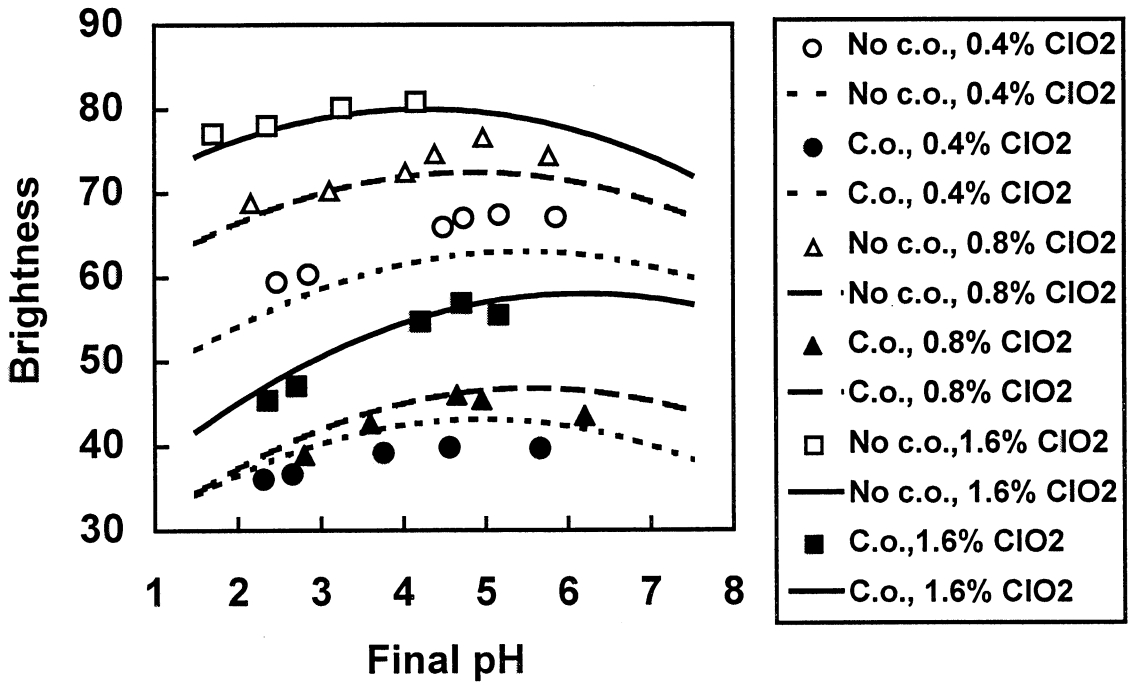


**Figure 4. Observed and predicted $D_1$ pH response in $D_0(EO)D_1$ at KF 0.15; C.o. = carryover.**

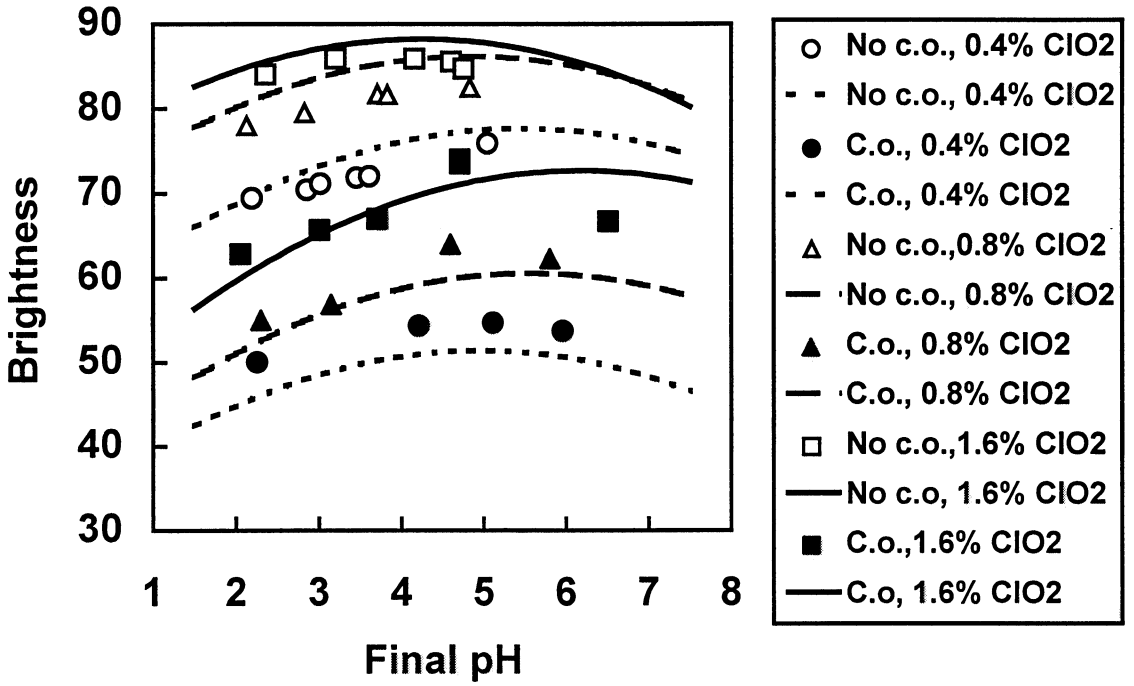


**Figure 5. Observed and predicted $D_1$ pH response in $D_0(EO)D_1$ at KF 0.25; C.o. = carryover.**

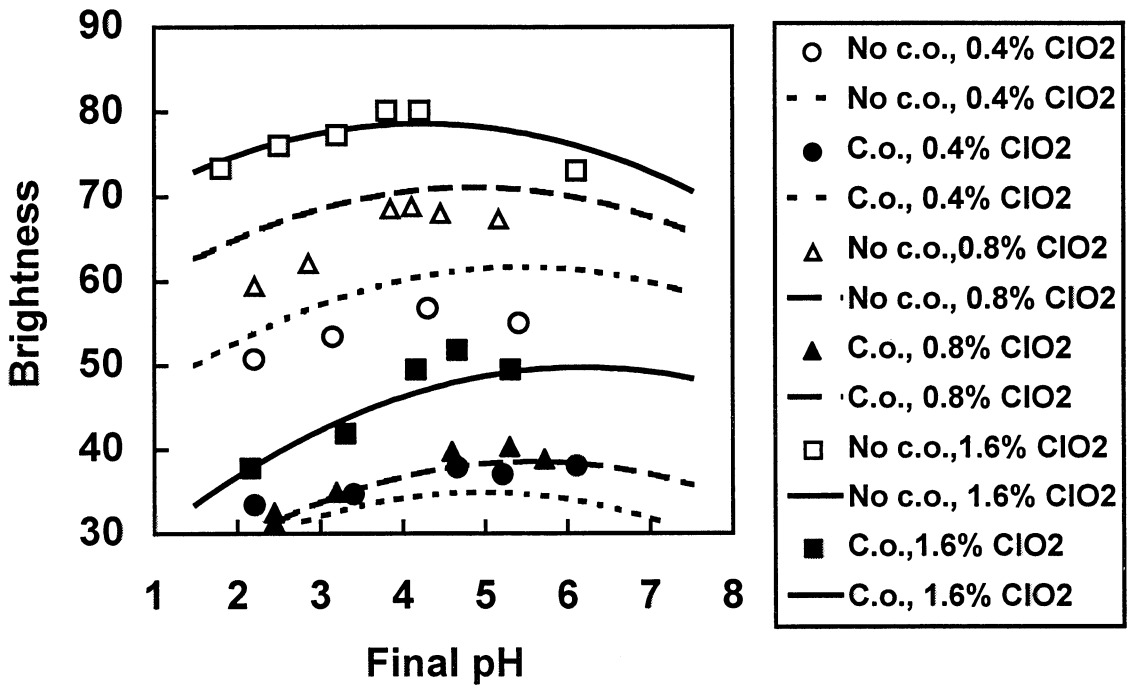


**Figure 6. Observed and predicted $D_1$ pH response in (DC) $(EO)D_1$ at KF 0.15; C.o. = carryover.**

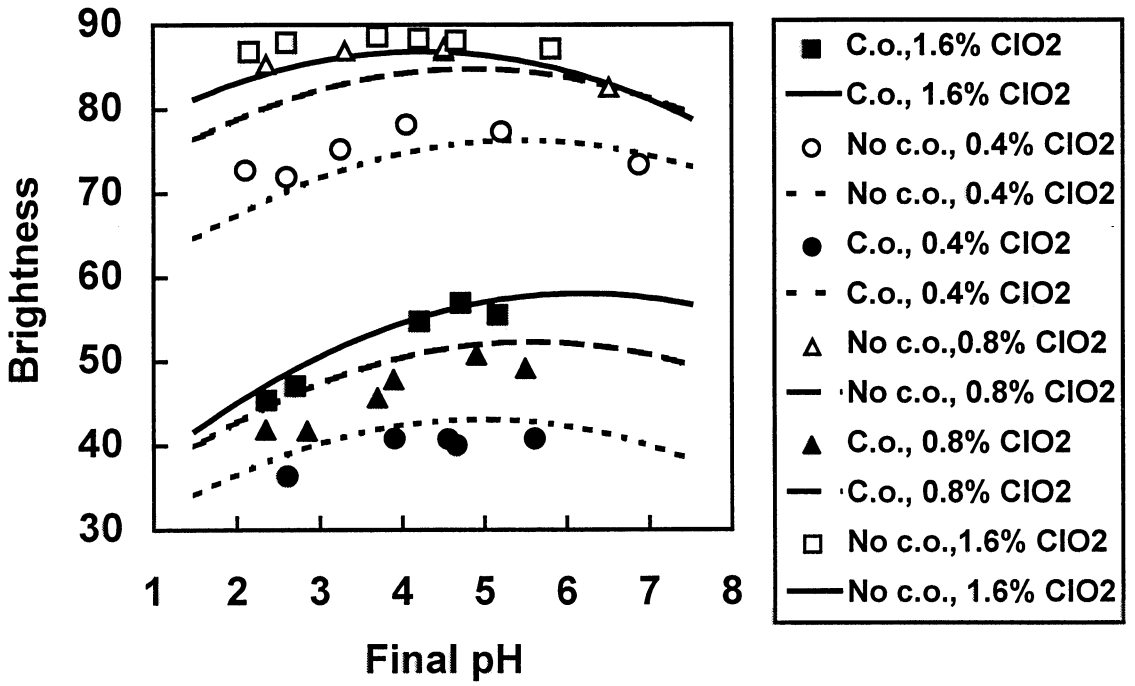


**Figure 7. Observed and predicted $D_1$ pH response in (DC) (EO)$D_1$ at KF 0.15; C.o. = carryover.**

### *Summary and Conclusions*

Analysis of the data to date shows that carryover increases the (EO) kappa number under all conditions of substitution and KF studied. At low KF, carryover has about the same effect on $D_0$ and (DC) bleaching. However, at high KF, carryover has significantly less effect on $D_0$ stage than on (DC). It is hypothesized that this is due to the presence in the dissolved organic black liquor solids of a fraction which is unreactive toward $ClO_2$ but reactive toward $Cl_2$.

Final brightness is higher for $D_0$ than for (DC) when carryover is high, and the optimum $D_1$ exit pH is higher at low KF than at high KF and higher in the presence of carryover than in its absence, both of these effects being greater for ECF than for bleaching at the lower substitution level.

## Effects of Pulping and Bleaching Processes on Pulp and Fiber Properties

### *Introduction*

A joint project between the Chemical and Biological Sciences (CBSD) and Fiber and Paper Physics (FFPD) Divisions has been initiated to characterize the effects of delignification and bleaching processes on fiber properties. The initial work has been defined to include conventional kraft batch pulping, oxygen delignification, and both CED and DED bleaching.

Kraft pulps from southern pine chips have been prepared at Kappa nos. of 94, 29, and 17and selected pulps have been further delignified by medium-consistency oxygen as described below. The 29 and 17 Kappa pulps and the oxygen delignified pulps will be bleached with both CED and DED sequences.

The extent of fiber property and strength changes imparted by the delignification and bleaching processes will be examined by FFPD.

## Pulping

Kraft pulps were prepared from a sample of southern pine chips acquired from a mill and screened on a Williams round hole chip screen at IPST. The $+^1/_4$ " and -1" fractions were retained for all cooks. Pulping was done in a 10 L M/K digester with external liquor circulation and heating. All cooks were done at a 4:1 liquor:wood ratio, heat-up from 100 to 170°C in 90 minutes, and time at 170°C varied for a desired H-factor. The cooking results are shown in Table 7.

**Table 7. Kraft Cooking Results**

| Active Alkali % | Sulfidity % | H-factor | Total Yield % | Screened Yield % | Kappa No. |
|---|---|---|---|---|---|
| 17.5 | 30 | 400 | 52.7 | 50.3 | 94.4 |
| 18.8 | 30 | 1250 | 45.1 | 44.8 | 30.1 |
| 18.8 | 30 | 1250 | 42.9 | 42.0 | 29.2 |
| 18.8 | 30 | 1250 | 44.1 | 42.3 | 29.0 |
| 18.8 | 30 | 1250 | 44.3 | 43.9 | 27.3 |
| 18.8 | 30 | 1250 | 43.4 | 43.6 | 29.6 |
| 18.8 | 30 | 1250 | 44.3 | 43.0 | 30.0 |
| 25.0 | 25 | 1250 | 42.4 | 42.0 | 17.0 |

After cooking the chips were removed from the digester in a basket. The 94 Kappa chips were defibered by refining in a 12" laboratory disc refiner at 0.020" gap. The other pulps were defibered by diluting in a tank and agitating. The defibered pulps were then screened on a Sprout Waldron flat screen with 0.006" slots. The accepts and rejects were collected separately and the dry weight determined for screened yield and % reject determinations.

Multiple cooks for the 30 Kappa target were done to provide enough pulp for a series of oxygen delignification runs.

## Oxygen Delignification

Oxygen delignification was done with a composite sample of the 30 Kappa kraft cooks. The composite pulp sample had a Kappa no. of 28.1. All runs were done in a pressurized reactor with a horizontal shaft mixer. The constant conditions were 10% consistency, 100°C, 90 psig $O_2$, 60 minutes, and 0.05% $Mg^{+2}$. The NaOH dosage was adjusted to achieve different degrees of delignification. The results are shown in Table 8. Three runs at each set of conditions were done to provide enough pulp for bleaching and testing. The pulps from each set were composited for further testing.

The greatest degree of delignification achieved was 62% at a Kappa no. of 10.7. This was somewhat higher than the desired final Kappa no. of 9. No further runs were done to reach a lower Kappa no. because of a shortage of brownstock.

## Bleaching

Bleaching is underway of the 28 and 17 Kappa brownstocks and each of the oxygen delignified pulps with both CED and DED sequences. The bleaching conditions are shown in Table 9.

**Table 8. Oxygen Delignification Results**

| NaOH % | Initial pH | Final pH | Yield % | Kappa No. | Delignification % | Composite Kappa No. |
|---|---|---|---|---|---|---|
| 0.8 | 11.92 | 9.27 | 99.76 | 19.9 | 29.2 | |
| 0.8 | 11.79 | 9.16 | 99.20 | 20.7 | 26.3 | 20.4 |
| 0.8 | 11.87 | 9.10 | 99.04 | 20.6 | 26.7 | |
| 1.45 | 12.34 | 9.43 | 98.48 | 15.9 | 43.4 | |
| 1.45 | 12.35 | 9.33 | 98.40 | 15.7 | 44.1 | 15.7 |
| 1.45 | 12.35 | 9.24 | 98.52 | 15.6 | 44.5 | |
| 2.30 | 12.64 | 9.70 | 97.44 | 12.0 | 57.3 | |
| 2.30 | 12.67 | 9.83 | 96.84 | 12.1 | 57.3 | 12.1 |
| 2.30 | 12.65 | 9.90 | 96.28 | 12.1 | 56.9 | |
| 2.70 | 12.71 | 9.78 | 96.84 | 10.6 | 62.3 | |
| 2.70 | 12.70 | 9.67 | 97.52 | 10.7 | 61.9 | 10.7 |
| 2.70 | 12.70 | 9.63 | 97.68 | 10.7 | 61.9 | |

**Table 9. Bleaching Conditions**

| | C or D | E | D |
|---|---|---|---|
| Consistency, % | 2.5 | 10 | 10 |
| Temperature, °C | 45 | 70 | 70 |
| Time, min. | 30 | 60 | 180 |
| Chemical | 0.2 KF | 0.55x act. $Cl_2$ | 1.2% $ClO_2$ |

## Fiber Properties

Fiber properties will be tested by the Fiber and Paper Physics Division as part of the dues-funded project F024. This will include refining studies in a PFI mill followed by handsheet and fiber evaluations. A summary of the pulps prepared for this study is shown in Table 10. There are 19 samples total. Not all of the fiber characterization tests will be done on every sample.

Each of the pulps for testing will be treated with a solution containing $Ca^{+2}$ to produce samples that are identical in ion content.

Characterization of the pulps will include carbohydrate and sugar analysis. Refining will be carried out in the PFI mill using CPPA method C.7 and testing of the refined pulps will include freeness, fines content, fiber length and curl, water retention value (WRV) and surface area. In addition, iron and palladium

staining techniques will be used to observe structural changes in the beaten fibers. Testing of handsheets will include zero span tensile, scattering coefficient, porosity, and elastic and failure properties.

**Table 10. Pulps for Testing**

| Pulp | Kappa no. | CED | DED |
|---|---|---|---|
| Conventional Kraft | 94.4 | - | - |
| Conventional Kraft | 28.1 | yes | yes |
| Conventional Kraft | 17.0 | yes | yes |
| Kappa 28 $\Rightarrow O_2$ | 20.4 | yes | yes |
| Kappa 28 $\Rightarrow O_2$ | 15.7 | yes | yes |
| Kappa 28 $\Rightarrow O_2$ | 12.1 | yes | yes |
| Kappa 28 $\Rightarrow O_2$ | 10.7 | yes | yes |

# Rapid $D_0$ Bleaching (With Project 4201)

## *Introduction*

Earlier, it was shown[1] that, in an OD(EO) sequence, a one-minute D stage achieved 84% of the delignification of a 30-minute stage while generating only 42% of the AOX. Further work was done (1) to demonstrate that fully bleached brightness could be achieved after a shortened $ClO_2$ delignification stage, (2) to evaluate the effect of shortening the $ClO_2$ delignification stage on the AOX generated downstream in the necessarily more vigorous $ClO_2$ brightening stage, and (3) to determine whether the beneficial effects observed earlier persisted when the kappa factor is decreased. Brightness development in the $OD_0(EOP)D_1$ sequence was only slightly affected by reducing the kappa factor from 0.25 to 0.10. At 0.25 kappa factor, decreasing the $D_0$ retention from 30 min. to 1 min. decreases fully bleached brightness by about 3 points at the same $D_1$ charge. In contrast, the corresponding effect at 0.10 kappa factor is less than one point. It was also apparent that, when the retention time is one minute, fully bleached brightness is almost independent of kappa factor over the range 0.10 to 0.25. It was concluded that there is no need for a $D_0$ bleach tower in low kappa factor ECF bleaching. Although the beneficial effect on full-sequence effluents was less than in the delignification partial sequence investigated earlier, a significant effect was observed at low kappa factor, where decreasing the $D_0$ retention time from 30 min. to 1 min. decreased AOX by 30% and $CL/C_{100}$ by 20%.

Further work was done on low-kappa number, otherwise conventional, non oxygen-delignified brownstock using a D(EOP)D(EP)D sequence to establish the feasibility of operating without a $D_0$ tower when full bleaching of conventional pulp is the objective. It showed that a $D_0$ retention time of 1 minute gives a $D_1$ brightness that is only two points lower than a $D_0$ retention time of 25 minutes. Furthermore when bleaching to high brightness in a five-stage sequence, the chemical consumption is almost the same as when a retention time of 25 minutes is used in $D_o$. At the same time substantial benefit could be realized by using the former $D_0$ tower elsewhere in the sequence, for a net gain in bleaching economy and a net reduction in AOX generation.

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[1] Schwantes, T.A. and McDonough, T.J., The effect of D stage reaction time on the characteristics of whole effluents and effluent fractions from D(EO) bleaching of oxygen delignified softwood kraft pulp, Preprints, 1994 International Pulp Bleaching Conference, Vancouver, B.C., June, 1994.

When these laboratory experiments were completed, it was apparent that an important unanswered question remained: Could the same benefits be achieved in a mill environment as in the idealized laboratory environment? It seemed likely that they could but the possibility existed that the degree of mixing achieved in industrial mixers would be less than in the laboratory and insufficient to allow the $D_0$ tower to be eliminated. A mill trial was clearly needed. Such a trial has now been completed in a member company mill.

## *Experimental*

The bleaching line where the experiments were conducted was in a mid-Atlantic kraft mill pulping Virginia pine. The mill uses only $ClO_2$ in the first stage of bleaching and has available two mixers, the first being a static mixer and the second a Sunds high shear mixer. A sampling point is available, 61 seconds downstream from the first mixer and 26 seconds downstream from the second.

The first of two sampling episodes was conducted on January 15, 1998, during a period when the mill was applying 1.63% $ClO_2$ to pulp having an unbleached kappa number of 27.6 (KF 0.155) and operating at a production rate of 275 tpd (close to capacity). The consistency after chemical addition was 3.2% and the stock temperature was 112°F. For the trial, the entire flow of $ClO_2$ was directed to the static mixer, 61 seconds upstream of the sampling point. The second series of samples was taken on January 16 during a period when all conditions were the same as during the first series, except that the entire $ClO_2$ flow was directed to the Sunds high shear mixer, 26 seconds upstream of the sampling point.

During each sampling period, the following procedure was used: A plastic wide mouthed jar with a screw cap was used to collect each sample. Prior to collecting the first one, 600 mL 10 g/L $Na_2SO_3$ was added to one of the jars before using it to collect a sample of about 2L of stock. The jar was immediately capped and shaken, then put aside while the other samples were collected. Another set of four samples was then taken. Each was collected in a jar containing no $Na_2SO_3$, a stopwatch was started at the time of sampling, and the jar containing the sample was immediately capped. After a specified time had elapsed (nominally 30, 60, 120, or 240 seconds), the cap was removed and 600 mL 10 g/L $Na_2SO_3$ was added, after which the jar was quickly recapped and vigorously shaken. The purpose of this set of samples was to obtain extracted kappa number as a function of time of exposure to $ClO_2$. A second set of five samples was collected for the purpose of obtaining residual $ClO_2$ as a function of retention time. This set was collected by the same procedure as the kappa number set, except that the $Na_2SO_3$ was replaced by excess acidified KI. The sampling episode was completed by taking a sample of unbleached pulp and a sample of the pulp exiting the extraction tower between the tower and the extraction stage washer. Retention times in the $D_0$ and (EO) towers were both approximately one hour. During the Jan. 16 episode, an additional sample was taken at the outlet of the Sunds high shear mixer, immediately after $ClO_2$ injection.

After all the samples had been collected from the sampling point downstream of the mixers, they were taken back to the mill lab for processing. Each of the first set was washed and subjected to a laboratory E stage (2.2 % NaOH, 10% consistency, I h at 70°C). The residual samples were titrated with standard $Na_2S_2O_3$.

## *Results and Discussion*

The results are shown in Table 11 and Figures 8 and 9. It is apparent that, during both sampling periods, extensive delignification and $ClO_2$ consumption had already occurred by the time the first sample was taken. Using the kappa number of the pulp exiting the mill's extraction stage as a benchmark $ClO_2$ retention times of 30, 60 and 120 seconds gave, after extraction, relative degrees of delignification of 87, 90 and 92%, respectively. Since these values are comparable to those we have obtained under similar conditions in the laboratory, we conclude that the industrial scale mixers, both static and dynamic, can give sufficiently good mixing to make Rapid $D_0$bleaching industrially feasible.

## *Summary and Conclusions*

Samples were taken immediately downstream of mixers in which $ClO_2$ was added to unbleached pine kraft in a full scale operating bleach plant. Analysis of the samples showed that retention times of 30, 60 and 120 seconds gave, after extraction, 87, 90 and 92% of the delignification achieved in the mills $ClO_2$ delignification ($D_0$) and extraction stages, each of which has a retention time of approximately one hour. It was concluded that the industrial scale mixers, both static and dynamic, can give sufficiently good mixing to make Rapid $D_0$bleaching industrially feasible.

**Table 11. Results of Analysis of Pulp Samples Collected Downstream of Mill $ClO_2$ Mixers**

| Date | Sampling Time | Retention Time, sec. | Residual $ClO_2$, % o.d.p. | Extracted Kappa Number | Percent of Final DE Delignification |
|---|---|---|---|---|---|
| Jan. 15 | 15:29 | 61 | | 8.0 | 92 |
| | 15:30 | 96 | | 8.1 | 92 |
| | 15:32 | 121 | | 8.1 | 92 |
| | 15:33 | 181 | | 7.4 | 95 |
| | 15:36 | 301 | | 6.9 | 98 |
| | 15:38 | 61 | 0.22 | | |
| | 15:55 | 91 | 0.20 | | |
| | 15:56 | 121 | 0.18 | | |
| | 15:59 | 181 | 0.11 | | |
| | 16:02 | 301 | 0.09 | | |
| | 16:12 | 0 | | 27.6 | |
| | 18:18 | 3600 | | 6.4 | |
| Jan. 16 | 8:50 | 26 | | 9.2 | 87 |
| | 8:51 | 61 | | 8.9 | 88 |
| | 8:53 | 86 | | 8.6 | 90 |
| | 8:55 | 146 | | 8.4 | 91 |
| | 8:58 | 266 | | 7.9 | 93 |
| | 9:00 | 26 | 0.27 | | |
| | 9:03 | 56 | 0.23 | | |
| | 9:06 | 86 | 0.20 | | |
| | 9:08 | 146 | 0.13 | | |
| | 9:11 | 266 | 0.09 | | |
| | 10:02 | 2 | | 11.1 | |
| | 11:00 | 0 | | 27.5 | |
| | 11:40 | 3600 | | 6.4 | |

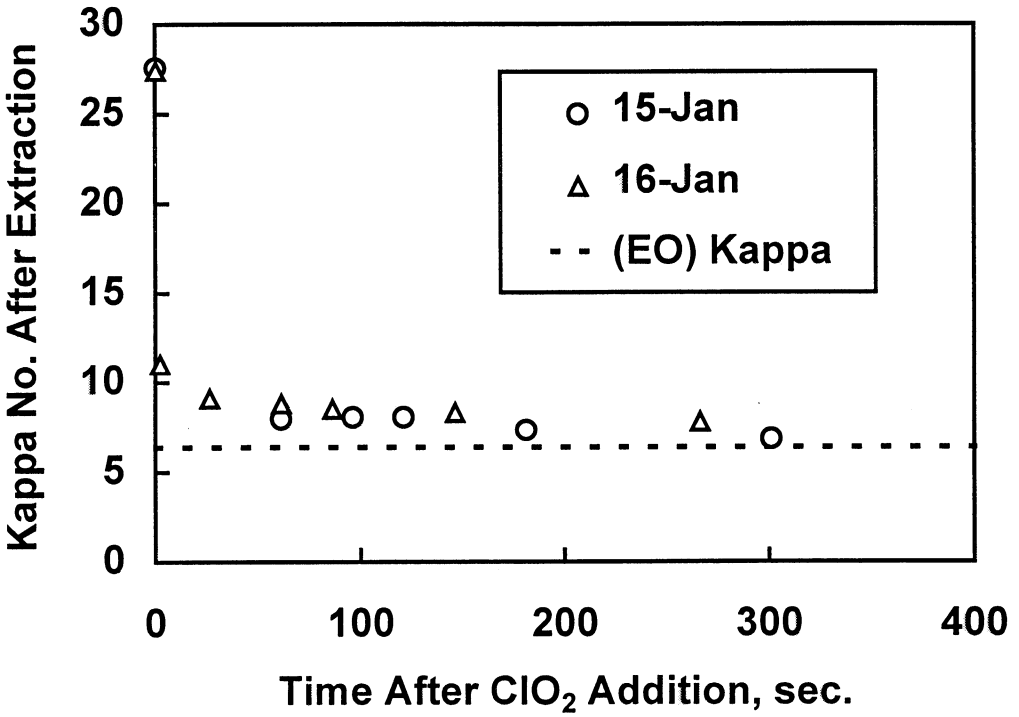


Figure 8. Kappa no. vs. retention time for pulp samples collected downstream of mill $ClO_2$ mixers.

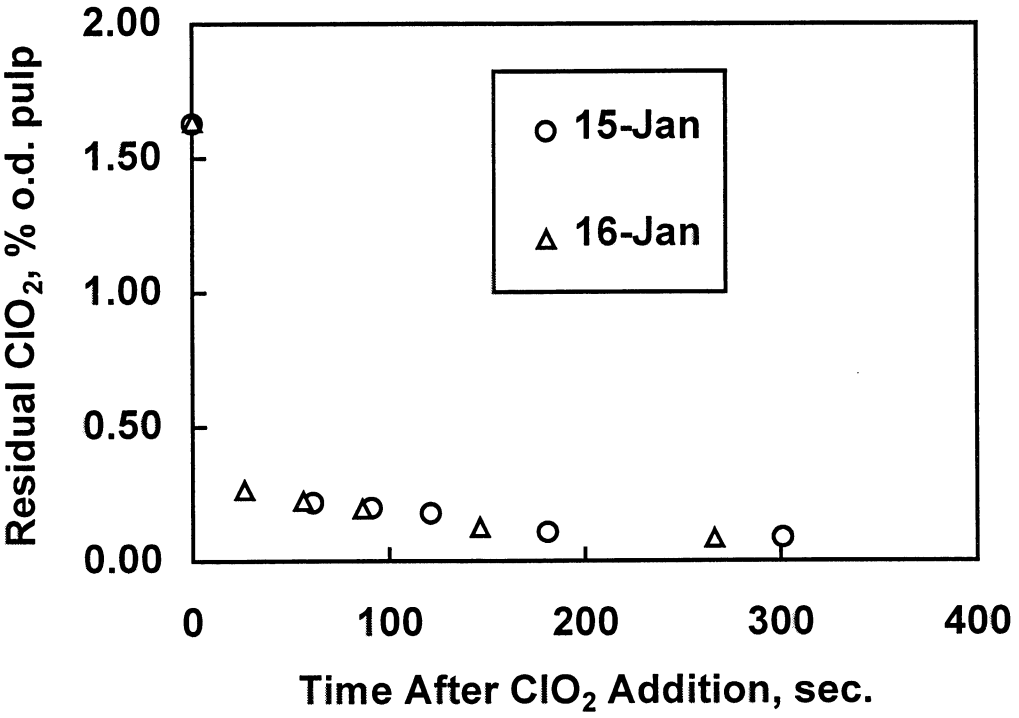


Figure 9. Residual $ClO_2$ vs. retention time for pulp samples collected downstream of mill $ClO_2$ mixers.

# Rapid $D_0$ Bleaching of Lo-Solids® and Conventional Pulps Over a Range of Unbleached Kappa Numbers (With Project 4159)

## *Introduction*

We have examined the results of applying Rapid $D_0$ bleaching in the delignification of a series of softwood kraft pulps prepared under conventional conditions and conditions that correspond to Lo-Solids® (LS) cooking, a modified kraft pulping process designed to allow delignification to be extended to low kappa numbers without loss of pulp quality. Pulps were prepared at several different kappa number levels. This was done in conjunction with a study of effects of $ClO_2$ delignification on residual lignin structure. In this context, Rapid $D_0$ was of interest because the short retention time is expected to yield bleached pulps having lignins whose structural features are unaffected by secondary reactions. The study also served to evaluate the dependence of Rapid $D_0$ delignification on kappa number and pulp type.

## *Experimental*

### Kraft Pulping

The kraft pulping experiments were performed at Alhstrom's pilot facilities in Glenns Falls, NY. Established procedures were used to simulate conventional and extended modified continuous (i.e., Lo-Solids®) cooking. Table 12 highlights some of the pulping parameters employed and pulp properties.

**Table 12. Pulping conditions and pulp properties from CK and EK pulps.**

| | Conventional Kraft Pulps (CK) | | | Lo-Solids® (LS) Pulps | | |
|---|---|---|---|---|---|---|
| Kappa # | 33.0 | 21.3 | 14.7 | 29.3 | 19.1 | 16.0 |
| Viscosity, mPa.s | 32.6 | 22.6 | 13.3 | 43.4 | 25.5 | 19.2 |
| Max. Temp., °C | 168 | 170 | 171 | 160 | 166 | 170 |
| H-Factor | 1201 | 1999 | 3496 | 2003 | 3362 | 4489 |
| Total EA Consumed, % on wood | 14.8 | 15.4 | 16.7 | 14.1 | 15.0 | 16.6 |

### Rapid $D_0$ Stage

Employing the quantum reactor, a 3% consistency pulp suspension was heated to 45°C and the pH was adjusted to either 5.0 or 4.0 for kappa factor 0.20 and 0.05 $ClO_2$ bleaching experiments, respectively. $ClO_2$ (kappa factor of either 0.05 or 0.20) was added to the quantum reactor, the pulp was mixed for 30 sec at 15 Hz and the mixer was then stopped for 30 sec., after which a quenching solution of aqueous $Na_2SO_3$ (mass $Na_2SO_3$ added = mass applied $ClO_2$ x 4.67 ) was injected. The pulp mixture was then stirred for an additional 30 sec., filtered, and characterized.

### (EO)-Stage

The pulp from the $D_0$ stage was thickened to 25% consistency, without washing, thoroughly disintegrated and added to a pin mixer. The consistency was adjusted to 10% and the pulp was then extracted under

typical (EO) conditions: NaOH charge was chosen to yield a terminal pH of 10.7-11.5. The (EO) stage was performed at 70°C for 60 min. The initial $O_2$ pressure was 60 psig and this was decreased 10 psig every 5 min. At the end of the (EO) stage, the pulp consistency was adjusted to 3%, the effluents were collected, and the pulp was thoroughly washed.

## *Results and Discussion*

The results of the bleaching studies are summarized in Table 3.

**Table 13. Rapid $D_0$ Bleachability of CK and LS Pulps**

| Pulp and Kappa No. | KF | TAC | Δ Kappa | TAC/Δ Kappa |
|---|---|---|---|---|
| CK -32.4 | 0.05 | 1.62 | D - 5.9 | 0.274 |
| | | | EO-13.6 | 0.119 |
| CK -32.4 | 0.20 | 6.48 | D - 15.3 | 0.423 |
| | | | EO-24.3 | 0.267 |
| CK-21.3 | 0.20 | 4.26 | D - 9.2 | 0.463 |
| | | | EO-15.3 | 0.278 |
| CK-14.7 | 0.20 | 2.94 | D - 6.5 | 0.452 |
| | | | EO-10.6 | 0.277 |
| LS-29.3 | 0.05 | 1.46 | D - 5.1 | 0.286 |
| | | | EO-13.0 | 0.112 |
| LS-29.3 | 0.20 | 5.86 | D - 13.7 | 0.428 |
| | | | EO-22.2 | 0.264 |
| LS-19.1 | 0.20 | 3.82 | D - 8.8 | 0.434 |
| | | | EO-14.6 | 0.262 |
| LS - 15.6 | 0.20 | 3.12 | D - 6.9 | 0.452 |
| | | | EO-11.8 | 0.264 |

The results summarized in Table 3 indicate that the conventional pulps exhibited only slightly improved bleachability at higher lignin contents when the $ClO_2$ retention time is kept short. The LS pulps were equally bleachable at high and low lignin contents under these conditions. These results differ somewhat from those of earlier studies by our group, indicating that the decreased bleachability of low-kappa pulps at normal $D_0$ retention times is related to inhibition of reactions that occur after the initial phase.

The LS pulps were modestly easier to delignify than the conventional pulps, requiring a $ClO_2$ charge that was an average of 4% lower than in the case of CK for a given kappa number reduction measured after the (EO) stage. The TAC/Δκ values were larger than normally observed at normal retention times in the $D_0$ stage because no credit was taken for the unutilized residual remaining after only one minute. In order to limit the $D_0$ reaction time to exactly one minute, it was necessary to stop the reaction by injection of sulfite, which destroyed the residual and precluded its measurement. It is for this reason that, in practical applications, low kappa factors are recommended for Rapid $D_0$.

### *Summary and Conclusions*

Rapid $D_0$ bleaching is applicable to conventional and Lo-Solids® and to pulps prepared at unusually low kappa number levels. Unlike conventional $ClO_2$ delignification, Rapid $D_0$ delignification does not consume more active chlorine per unit of lignin removed as the unbleached kappa number is decreased.

## Vapor Phase Bleaching of Hardwood and Softwood Kraft (With Project 4159)

### *ABSTRACT*

Laboratory vapor phase $ClO_2$ delignification experiments were performed on hardwood pulps made from sweetgum by laboratory simulations of both conventional and RDH kraft pulping. A smaller number of experiments were conducted on pulps made from southern pine by laboratory simulations of conventional kraft pulping. All experiments consisted of $D_0$(EO) bleaching followed by determinations of kappa number and analysis of the individual stage filtrates for AOX, as well as chloride, chlorate and chlorite ions. For comparison, control experiments were done in which the $ClO_2$ was applied at low consistency, in the conventional manner. In bleaching the hardwood pulps, vapor phase delignification was remarkably more efficient, but generated markedly larger quantities of AOX than the conventional process, which itself generated much more AOX than expected on the basis of earlier softwood pulp bleaching data. These observations, together with analyses of the bleaching filtrates, are consistent wit the hypothesis that $ClO_2$ partially decomposes to $Cl_2$ in the vapor phase before reacting with the pulp. In the case of southern pine kraft pulps, there was a much smaller improvement in delignification efficiency in going from low consistency to vapor phase bleaching. Qualitatively similar observations were made with regard to the softwood pulps, but the trends were generally less pronounced than in the case of the hardwood pulps. Differences in the structure of hardwood pulp residual lignin after conventional and vapor phase bleaching were slight. This may indicate that the superior bleaching efficiency of the vapor phase process is due to diminished importance of reactions that occur between active chlorine compounds and dissolved organic byproducts.

### *Results and Discussion*

The complete text of a paper to be presented at the 1998 International Environmental Conference is attached as Appendix 1.

## Chlorine Dioxide Bleachability of Pine Kraft Pulps Made With Controlled Liquor Concentration Profiles (With Project 4120)

### *ABSTRACT*

In an effort to assign a cause for the superior bleachability of pulps made by modified pulping processes, we have conducted systematic bleaching studies of southern pine pulps prepared with two types of controlled liquor concentration profiles. In one type, the alkali concentration, after an initial decrease, was maintained at a constant value. In the second type, the same kind of alkali profile was augmented by continuous liquor replacement to limit the concentrations of dissolved lignin and other reaction products. Neither type of profiling had any effect on the bleachability of the resulting pulps in the $D_0$(EO)$D_1E_2D_2$ bleaching sequence. Structural analyses of residual lignins showed that alkali profiled cooks gave residual lignins having slightly lower contents of phenolic groups, both uncondensed and condensed, as well as lower contents of aliphatic hydroxyl groups. These differences may contribute to the failure of the pulps from the profiled cooks to exhibit better bleachability than those from conventional cooks

### *Results and Discussion*

The complete text of a paper to be presented at the 1998 International Pulp Bleaching Conference is attached as Appendix 2.

## Effects of Washer Efficiency on Characteristics of Effluents from D(EPO)D Bleaching of a Softwood Kraft Pulp With Project (With Project 4106)

### *ABSTRACT*

We have conducted a systematic study of AOX, BOD, and COD released by bleaching southern pine kraft pulp in the $D_0(EPO)D_1$ sequence at a kappa factor of 0.20 and a $D_1$ stage $ClO_2$ charge of 1.2%. Measurements of all three parameters were made at three different levels of carryover of $D_0$ stage filtrate into the (EPO) stage and three different levels of carryover of (EPO) stage effluent into the $D_1$ stage, and the entire experiment was duplicated.

The combined AOX contributions of the $D_0$ and (EPO) stages amounted to 11.6% of the chlorine atoms applied in the $D_0$ stage, while the contribution of the $D_1$ stage amounted to 2.7% of the chlorine atoms applied in the $D_1$ stage. The combined AOX contributions of all three stages decreased when the $D_0$ stage carryover was increased from 0 to 10% and was unaffected by (EPO) stage carryover. With perfect washing between stages, COD contributions to the combined bleach plant filtrates by the $D_0$, (EPO) and $D_1$ stages were, respectively, 14.1, 39.8, and 2.9 kg/odumt. The combined COD contributions of all three stages was relatively unaffected by a low level (5%) of $D_0$ stage carryover, but a higher level (10%) resulted in an overall COD increase of 2 kg/odumt. Increasing (EPO) stage carryover from 0 to 30% decreased total COD by 3 kg/t. With perfect washing between stages, BOD contributions to the combined bleach plant filtrates by the $D_0$, (EPO), and $D_1$ stages were, respectively, 3.8, 7.0, and 2.2 kg/odumt. No significant effect of carryover levels on the total BOD release could be detected.

### *Results and Discussion*

The complete text of a paper to be presented at the 1998 International Environmental Conference is attached as Appendix 3.

## Effective Alkali and Pulping Temperature Effects on the Bleachability of Birch and Maple Kraft Pulps (With Project 4120)

### *Introduction*

The objective of this work was to study the effect of individual pulping variables on the ECF bleachability of hardwood kraft pulps at constant kappa number. This was done so that a comparison could be made between differently prepared pulps having roughly the same starting lignin content to gain insight into how and to what extent the bleachability of the pulps is affected by individual pulping variables. The two hardwood species that we chose to study were Maple and Birch.

### *Results and Discussion*

A report describing this work is attached as Appendix 4.

# APPENDIX I

# Studies of Chlorine Dioxide Delignification: Vapor Phase Bleaching of Hardwood and Softwood Kraft Pulps

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## ABSTRACT

Laboratory vapor phase $ClO_2$ delignification experiments were performed on hardwood pulps made from sweetgum by laboratory simulations of both conventional and RDH kraft pulping. A smaller number of experiments were conducted on pulps made from southern pine by laboratory simulations of conventional kraft pulping. All experiments consisted of $D_0$(EO) bleaching followed by determinations of kappa number and analysis of the individual stage filtrates for AOX, as well as chloride, chlorate and chlorite ions. For comparison, control experiments were done in which the $ClO_2$ was applied at low consistency, in the conventional manner. In bleaching the hardwood pulps, vapor phase delignification was remarkably more efficient, but generated markedly larger quantities of AOX than the conventional process, which itself generated much more AOX than expected on the basis of earlier softwood pulp bleaching data. These observations, together with analyses of the bleaching filtrates, are consistent wit the hypothesis that $ClO_2$ partially decomposes to $Cl_2$ in the vapor phase before reacting with the pulp. In the case of southern pine kraft pulps, there was a much smaller improvement in delignification efficiency in going from low consistency to vapor phase bleaching. Qualitatively similar observations were made with regard to the softwood pulps, but the trends were generally less pronounced than in the case of the hardwood pulps. Differences in the structure of hardwood pulp residual lignin after conventional and vapor phase bleaching were slight. This may indicate that the superior bleaching efficiency of the vapor phase process is due to diminished importance of reactions that occur between active chlorine compounds and dissolved organic byproducts.

## INTRODUCTION

"Vapor phase" delignification of unbleached kraft pulp consists of contacting it, at high consistency, with a gas stream containing $ClO_2$. This mode of $ClO_2$ application has been proposed as a means of achieving efficient delignification while simultaneously generating relatively small amounts of byproduct adsorbable organic halide (AOX).[1,2] Our interest in this process has been as part of a study of the interdependence of delignification efficiency, bleaching conditions, residual lignin structural changes and byproduct generation currently being funded by the U.S. Department of Energy through the Agenda 2020 Program, and by the Institute of Paper Science and Technology (IPST). Accordingly, we have conducted vapor phase $ClO_2$ delignification experiments in the laboratory and have followed them with determinations of residual lignin structural changes and effluent AOX. To date, the emphasis has been on hardwood pulps made from sweetgum by laboratory simulations of both conventional and RDH kraft pulping. Some experiments were also conducted on pulps made from southern pine by laboratory simulations of conventional kraft pulping.

## EXPERIMENTAL

**Bleaching.** Vapor phase $D_0$ stage bleaching was done by passing a stream of nitrogen and chlorine dioxide through a rotating spherical flask containing fluffed pulp at 30% consistency maintained at 60°C. The gas stream was generated by stripping $ClO_2$ from a 6.2 g/L solution containing a negligibly small amount of $Cl_2$. The flask containing $ClO_2$ solution, initially at 4°C, was placed in a 90°C water bath and the flow of $N_2$ was immediately started. An amount of $ClO_2$ solution containing 3 g $ClO_2$ was used in every case, and the amount of $ClO_2$ delivered to the reaction flask was controlled by controlling the $N_2$ flow rate and the duration of the experiment. For example, 2.92 g $ClO_2$ was delivered by passing $N_2$ through the solution for 10 min. at a flow rate of 6.5 L/min. The gas leaving the reactor was passed through 10% KI, which was subsequently titrated iodometrically to determine the amount of unreacted $ClO_2$. Hardwood pulps supplied with an amount of $ClO_2$ corresponding to a kappa factor of 0.20 consumed 77-91% of the applied $ClO_2$, depending on the unbleached kappa number. Kappa no. 30.7 softwood

kraft pulp, when supplied with an amount of $ClO_2$ corresponding to a kappa factor of 0.276, consumed 67%, an amount corresponding to a kappa factor of 0.184. For all pulps, the $ClO_2$ was completely consumed when the amount supplied corresponded to a kappa factor of 0.05.

Conventional $D_0$ stage bleaching was done in a Quantum reactor at 3% consistency and 45°C for 30 min. The mixer was turned on during $ClO_2$ addition and for 15 sec. thereafter, and for 5 seconds every 5 min. throughout the remainder of the bleaching period.

Both types of $D_0$ stage were followed by an (EO) stage conducted in a laboratory pin mixer at 10% consistency and 70°C for 60 min. The oxygen pressure was initially 60 psig. and was decreased by 10 psig. every 5 min.

Filtrate samples were collected immediately upon termination of each bleaching stage. After vapor phase $D_0$ stages and (EO) stages, the pulp was diluted to 3% consistency and thoroughly mixed before filtering. Samples for AOX determination were acidified to pH 2 with concentrated $HNO_3$. All samples were refrigerated pending analysis. Determinations of AOX were made according to EPA method 1650. Chloride, chlorate and chlorite were determined by capillary ion electrophoresis.

The unbleached pulps were prepared in the laboratory by standard methods. All of the hardwood pulps were prepared from fresh sweetgum chips at the laboratories of Beloit Corporation. A softwood pulp of 18.7 kappa number was prepared at IPST. The remaining softwood pulps were kindly provided through the courtesy of J. Jiang and K. Crofut of Ahlstrom Machinery, Inc., who prepared them from southern pine chips supplied by IPST.

**Lignin isolation.** The isolation of lignin from the kraft pulps was accomplished employing standard literature methods.[5] In brief, air-dried pulp (60 g oven-dry weight) was added to an aqueous 0.1 N HCl (146 ml 1 N HCl), p-dioxane (1300 ml freshly distilled) solution and this mixture was then refluxed for 2 hr. under an argon atmosphere. The mixture was then filtered, and the filtrate was filtered through celite. The solution was neutralized with sodium bicarbonate and concentrated under reduced pressure. After the filtrate was vacuum distilled to less than 10% of the original volume water was added (3 x 200 mL) and the mixture was reconcentrated under reduced pressure. The aqueous solution was then acidified pH to 2.5 with an aqueous 1 N HCl solution. The resulting precipitate was collected, washed several times with distilled water, and freeze-dried.

**Lignin NMR studies.** NMR data were acquired with a DMX 400 MHz Bruker spectrometer. Quantitative $^{31}P$-NMR experiments were performed following standard literature methods.[3]

## RESULTS AND DISCUSSION

Results indicative of $D_0(EO)$ delignification efficiency are contained in Table I for the hardwood pulps and in Table II for the softwood pulps. As shown in Table I, vapor phase delignification of the hardwood pulps was remarkably more efficient than conventional, low consistency bleaching. In spite of the fact that less $ClO_2$ was consumed in the vapor phase experiments, the kappa number after extraction was 50% lower. This is in agreement with Mendiratta's earlier observation that delignification at high consistency with a gaseous mixture of $ClO_2$, $O_2$, and water vapor gave much better delignification efficiency than conventional medium consistency delignification. In the present case, hardwood pulp delignification efficiency in the $D_0(EO)$ partial sequence, expressed as kappa number reduction per percent of active chlorine consumed, was 4.4-5.3 for the vapor phase $D_0$ stage, as compared to 3.0-3.9 for the low consistency $D_0$ stage.

In the case of the softwood pulps, as shown in Table II, there was a much smaller improvement in delignification efficiency in going from low consistency to vapor phase bleaching. This observation differs from those made earlier by Mendiratta[1] and Reeve[4], indicating that vapor phase delignification efficiency is sensitive to operating conditions, and perhaps also to unbleached pulp characteristics. In this regard, it is worth noting that we made no attempt to optimize the vapor phase $ClO_2$ stage, either for bleaching performance or effluent quality.

Several important observations not directly related to the comparison between vapor phase and conventional bleaching may also be made with regard to the data in Tables I and II. One confirms the observation, made previously in this laboratory and elsewhere, that delignification efficiency exhibits a modest decrease as unbleached kappa number is decreased. The data of Table II also reveal a very large effect of kappa factor on delignification efficiency, the efficiency being more than twice as high at kappa factor 0.05 than at 0.2. Finally, it is apparent that

**Table I. Hardwood Pulp Bleaching Data**

| Experiment | Process | Unbl.Pulp | | $D_0$ Stage | | | (EO) Stage | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Pulp Type | Kappa Number | Kappa Factor | Kappa Number | Delta Kappa/ TAC | NaOH Charge, % o.d.p. | Final pH | Kappa Number | Delta Kappa/ TAC |
| HCC1 | Conventional | Conv. | 11.4 | 0.200 | 6.2 | 2.3 | 2.5 | 12.4 | 4.2 | 3.2 |
| HCC2 | | | 15.2 | 0.200 | 7.9 | 2.4 | 2.0 | 12.0 | 5.2 | 3.3 |
| HCR1 | | RDH | 7.8 | 0.200 | 5.6 | 1.4 | 1.7 | 11.9 | 3.1 | 3.0 |
| HCR2 | | | 13.4 | 0.200 | 10.0 | 1.3 | 1.7 | 12.0 | 5.2 | 3.1 |
| HCR3 | | | 22.9 | 0.200 | 13.9 | 2.0 | 1.7 | 11.6 | 5.2 | 3.9 |
| HVC1 | Vapor Phase | Conv. | 11.4 | 0.181 | 4.2 | 3.5 | 1.7 | 11.8 | 2.3 | 4.4 |
| HVC2 | | | 15.2 | 0.171 | 5.3 | 3.8 | 1.7 | 11.8 | 2.5 | 4.9 |
| HVR1 | | RDH | 7.8 | 0.155 | 3.3 | 3.7 | 1.7 | 11.9 | 1.5 | 5.2 |
| HVR2 | | | 13.4 | 0.172 | 5.4 | 3.5 | 1.7 | 11.8 | 2.8 | 4.6 |
| HVR3 | | | 22.9 | 0.167 | 8.2 | 3.8 | 1.7 | 10.6 | 2.6 | 5.3 |

**Notes:** 1. $D_0$ stage conditions: For conventional bleaching, Quantum Mixer, 30 min., 45°C, 3% consistency, final pH 2.5-3.0. For vapor phase bleaching, rotating spherical glass reactor, 7-10 min., 60°C, 30% consistency, final pH 2.5-3.0.

2. (EO) stage conditions: Pin mixer, 60 min., 70°C, 10% consy., oxygen pressure initially 60 psig. and decreased by 10 psig. every 5 min.

there is little difference in $D_0$(EO) delignification efficiency between hardwood and softwood pulps, or between conventional and RDH pulps, at least over the ranges of kappa numbers investigated in this study. This suggests that the relative ease of bleaching of hardwood pulps has more to do with their lower unbleached kappa numbers than with any inherent difference in ease of lignin removal.

Information on the mechanisms of delignification and potential environmental effects was obtained by collecting and analyzing filtrates from each of the bleaching stages. The resulting data are presented in Tables III and IV. The yield figures shown in these tables represent the percentages of the chlorine atoms in the $ClO_2$ charged that are converted to the indicated species.

**Table II. Softwood Pulp Bleaching Data**

| Experiment | Process | Unbl. Pulp | | $D_0$ Stage | | | (EO) Stage | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Pulp Type | Kappa Number | Kappa Factor | Kappa Number | Delta Kappa/ TAC | NaOH Charge, % o.d.p. | Final pH | Kappa Number | Delta Kappa/ TAC |
| SCC1 | Conventional | Conv. | 18.7 | 0.050 | 14.2 | 4.8 | 1.2 | 11.2 | 10.2 | 9.1 |
| SCC2 | | | | 0.200 | 8.8 | 2.6 | 1.8 | 11.6 | 3.9 | 4.0 |
| SCC3 | | | 30.4 | 0.200 | 14.6 | 2.6 | 2.5 | 11.2 | 4.2 | 4.3 |
| SCC4 | | | 33.0 | 0.200 | 12.0 | 3.2 | 2.6 | 11.2 | 4.6 | 4.3 |
| SVC1 | Vapor Phase | | 30.7 | 0.050 | 26.4 | 2.8 | 2.5 | 12.2 | 15.8 | 9.7 |
| SVC2 | | | | 0.184 | 15.4 | 2.7 | 2.5 | 11.8 | 4.5 | 4.6 |

**Notes:** 1. $D_0$ stage conditions: For SCC1 and SCC2, Quantum Mixer, 30 min., 45°C, 3% consistency, final pH 2.3-2.8. For SCC3 and SCC4, Quantum Mixer, 45 min., 45°C, 10% consistency, final pH 2.0. For SVC1 and SVC2, rotating spherical glass reactor, 8-10 min., 60°C, 30% consistency, final pH 2.6-2.8.

2. (EO) stage conditions: Pin mixer, 60 min., 70°C, 10% consy., oxygen pressure initially 60 psig. and decreased by 10 psig. every 5 min.

Striking features of the hardwood data (Table III) are the markedly higher the rate of AOX generation in the vapor phase process than in the conventional one, the high levels of AOX in even the conventional process, and the decreased AOX yield when low kappa number pulps are bleached. These effects are also graphically shown in

Figure 1. Vapor phase delignification generated AOX at more than twice the rate of the conventional process, which, in turn, generated more than expected on the basis of a model based on a review of the literature on softwood bleaching with mixtures of $ClO_2$ and $Cl_2$.[5] The latter study showed that delignification of softwoods in the (DC)E partial sequence with mixtures of $ClO_2$ and $Cl_2$ rich in $ClO_2$ converted about 8% of the charged Cl atoms into AOX. The corresponding figures for $D_0$(EO) delignification of hardwood pulps from the present study (averages from Table III) are 14% for a low consistency $D_0$ stage and 33% for a vapor phase $D_0$ stage. Tentative conclusions are that hardwood pulps give a higher yield of AOX than softwoods, and that vapor phase delignification of hardwood pulps generates abnormally large quantities of AOX under the conditions employed in this study. The higher AOX levels in vapor phase delignification may be indicative of gas phase decomposition of $ClO_2$ prior to its reaction with the lignin in the pulp, which would also explain the higher delignification efficiency, because of the known superiority of $Cl_2$ - $ClO_2$ mixtures in this respect. The composition of the mixture of inorganic byproducts is consistent with this explanation, since the vapor phase filtrates contained somewhat lower concentrations of chloride ion, and a greater proportion of the chloride ion produced in the vapor phase process was released in the alkaline extraction stage. Both of these changes are to be expected when substitution assumes a greater role relative to oxidation. The vapor phase filtrates also contained markedly less chlorate ion (Figure 2), as would be expected if $ClO_2$ had decomposed to $Cl_2$ before reacting. Regardless of the mechanism, the lower rate of chlorate production is consistent with the higher delignification efficiency of the vapor phase process.

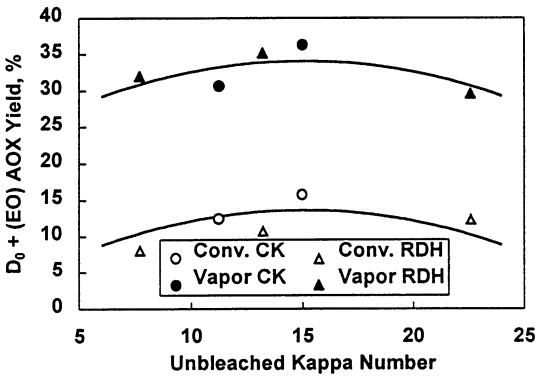


**Figure 1. Sum of AOX yields from analyses of $D_0$ (EO) stage filtrates**

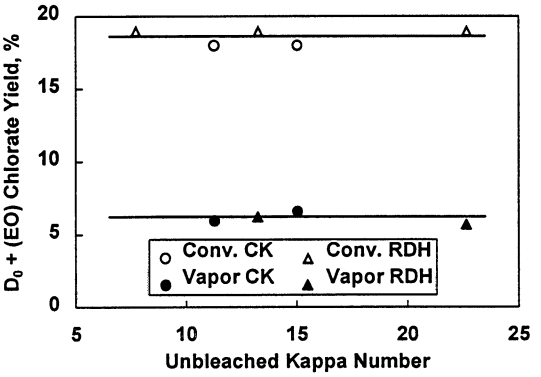


**Figure 2. Sum of chlorate yields from analysis of $D_0$ and and (EO) stage filtrates**

Qualitatively similar observations may be made with regard to the softwood pulp data presented in Table IV, but the trends were generally less pronounced than in the case of the hardwood pulps. Thus, the disparity between the rates of AOX generation in the vapor phase and conventional processes, though still great (18% vs 10%), was smaller than in the case of hardwoods (33% vs. 14%). The AOX levels for the conventional process were only slightly greater than predicted by the model referred to earlier, and the effect of kappa number on AOX yield was either absent or too small to be apparent. The reduction in chlorate yield associated with going from the conventional process to the vapor phase process, unlike the trends just mentioned, was just as pronounced for the softwood pulps as for the hardwoods. In addition, positive effects of increasing kappa factor on the yields of both AOX and chlorate ion was observed. Figures 3 and 4 illustrate these effects.

To elucidate the mechanisms of the conventional and vapor phase $ClO_2$ delignification processes residual lignin was isolated from the conventional kappa no. 15.2 hardwood pulp before bleaching, after the $D_0$ stage, and after the (EO) stage, for both the conventional and vapor-phase bleaching processes. The residual lignin was isolated using an acidic dioxane extraction procedure that has been employed by several researchers[6]. The resulting lignin was then purified, derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane and characterized by $^{31}P$ NMR.[3]

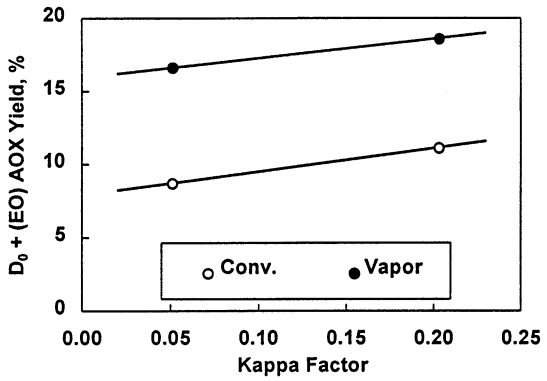


Figure 3. Sum of AOX yields from analyses of $D_0$ and (EO) stage filtrates from bleaching of softwood pulps.

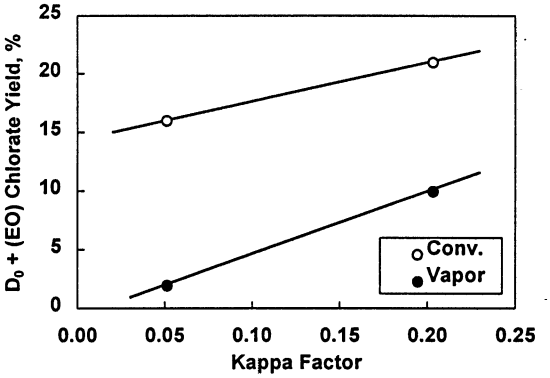


Figure 4. Sum of chlorate yields from analyses of $D_0$ and (EO) stage filtrates from bleaching of softwood pulps.

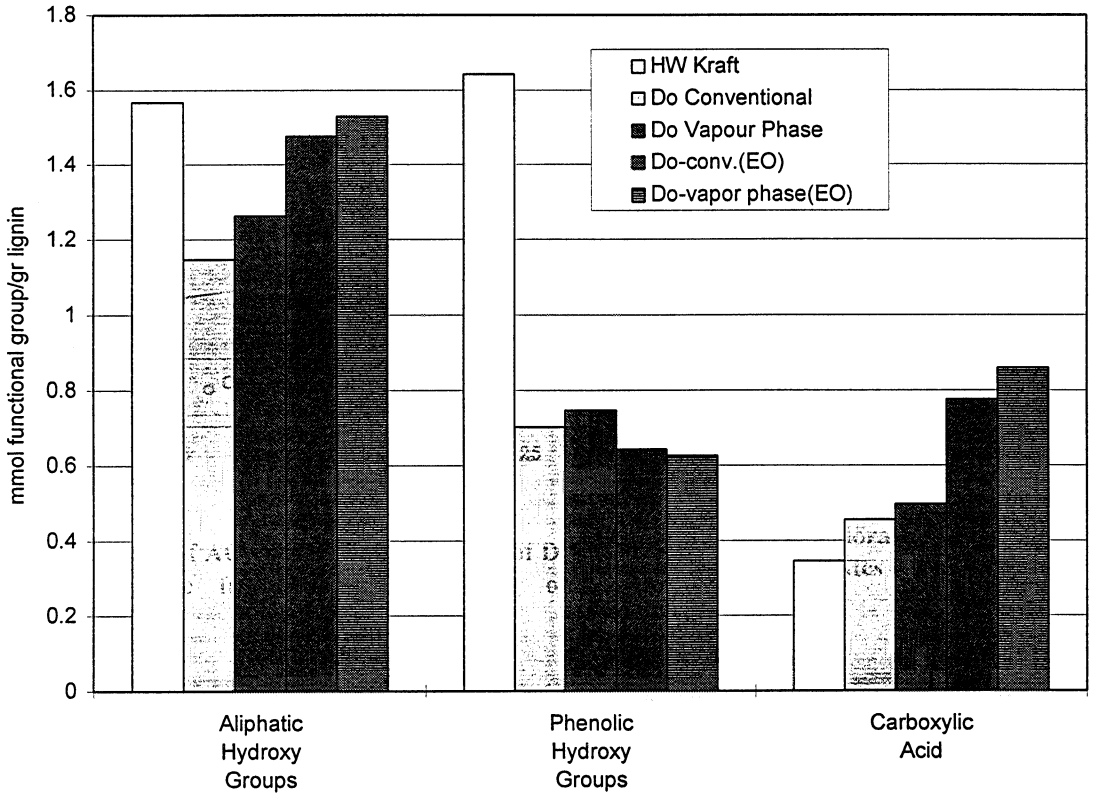


Figure 6. Changes in aliphatic, carboxylic, and phenolic hydroxy content for conventional hardwood kraft pulp (kappa # 15.2) bleached $D_0$, 0.20 k.f., with vapor phase and conventional conditions followed by an (EO) stage.

The results of this analysis are illustrated in Figure 6. As expected, the residual lignin was found to be enriched in acid groups as the brownstock pulp was treated with $ClO_2$ and subsequently alkaline extracted in an (EO) stage. Interestingly, the residual lignin isolated from the vapor phase $D_0$ and $D_0$(EO) pulps exhibit a slight enrichment in acid groups over the conventional $D_0$ bleached pulp. A slight decrease in aliphatic hydroxy group content after the $D_0$-stage could be potentially attributed to some oxidation of the side chain of lignin. Both the conventional and vapor-phase $D_0$ stages removed extensive amounts of phenolic groups from the residual lignin, which was expected since the phenolic group is the primary site of oxidation by chlorine dioxide.

The NMR methods employed in this study can further differentiate the phenolic groups into (a) syringyl, (b) condensed and (c) guaiacyl and demethylated phenolics. Figure 7 summarizes the results of this analysis for the lignins studied in this report. Although all three types of phenolic groups are removed during the Do bleaching stage, it is clear that the syringyl units are the most reactive towards chlorine dioxide. Interestingly, the loss of guaiacyl and condensed types of phenolic groups appears to occur in comparable amounts. This result differs from our previous studies in which we noted condensed phenolic groups to be resistant to oxidative bleaching agents.[7] The factors contributing to this trend will need to be further investigated so as to fully determine the mechanism of oxidative removal of condensed phenolics.

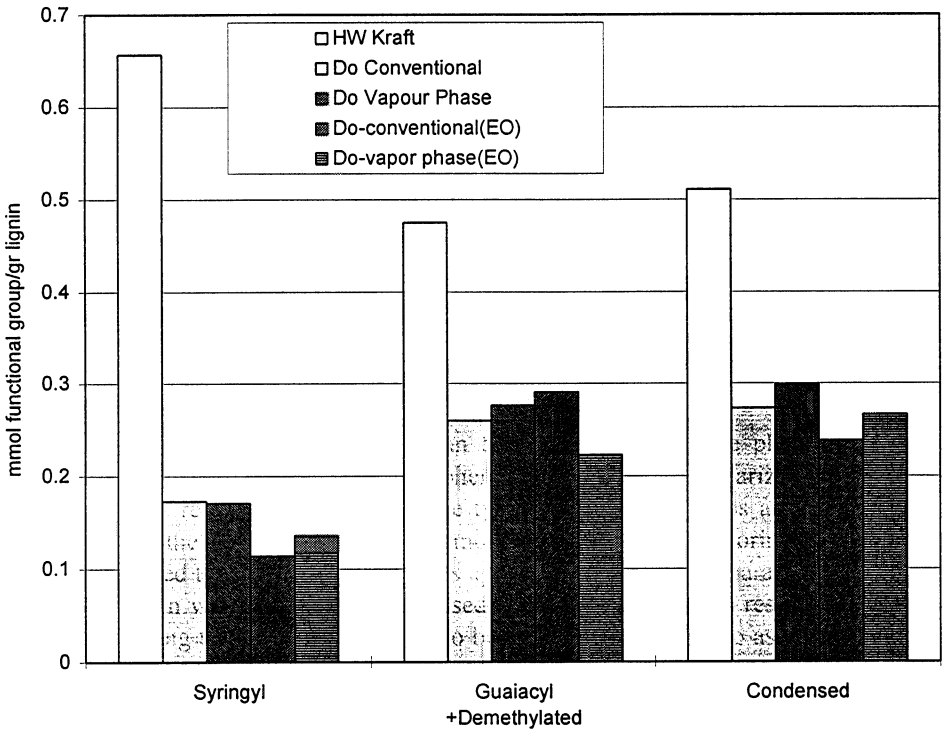


**Figure 6. Changes in syringyl, condensed, and guaiacyl/demethylated phenolic hydroxy units for conventional hardwood kraft pulp (kappa # 15.2) bleached $D_0$, 0.20 k.f., vapor phase and conventional, followed by an (EO) stage.**

**Table III. Fate of Chlorine in Hardwood Pulp Bleaching**

| | | Unbl. Pulp | | $D_0$ Stage | | | | | | (EO) Stage | | | | | Total | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Yields of Cl Cpds, Mole % $ClO_2$ | | | | | Yields of Cl Cpds, Mole % $ClO_2$ | | | | | Yields of Cl Cpds, Mole % $ClO_2$ | | | | |
| Expt. | Process | Pulp Type | Kappa Number | Kappa Factor | AOX, kg/t | AOX | $Cl^-$ | $ClO_3^-$ | $ClO_2^-$ | AOX, kg/t | AOX | $Cl^-$ | $ClO_3^-$ | $ClO_2^-$ | AOX, kg/t | AOX | $Cl^-$ | $ClO_3^-$ | $ClO_2^-$ | Total Cl Recovery, % |
| HCC1 | Conv. | Conv. | 11.4 | 0.200 | 0.541 | 11.9 | 44 | 16 | 1 | 0.037 | 0.8 | 8 | 1 | 4 | 0.571 | 12.7 | 52 | 18 | 5 | 87 |
| HCC2 | | | 15.2 | 0.200 | 0.834 | 13.7 | 47 | 17 | 1 | 0.136 | 2.2 | 8 | 1 | 2 | 0.960 | 16.0 | 55 | 18 | 3 | 92 |
| HCR1 | | RDH | 7.8 | 0.200 | 0.294 | 9.4 | 56 | 18 | 1 | 0.052 | 1.7 | 8 | 1 | m.i. | 0.261 | 11.1 | 64 | 19 | m.i. | 94 |
| HCR2 | | | 13.4 | 0.200 | 0.737 | 13.8 | 51 | 18 | 1 | 0.142 | 2.7 | 8 | 1 | m.i. | 0.589 | 16.4 | 59 | 19 | m.i. | 94 |
| HCR3 | | | 22.9 | 0.200 | 0.916 | 10.0 | 53 | 17 | 0 | 0.521 | 5.7 | 7 | 1 | m.i. | 1.152 | 15.7 | 60 | 19 | m.i. | 94 |
| HVC1 | Vapor | Conv. | 11.4 | 0.181 | 1.180 | 28.5 | 43 | 6 | 0 | 0.092 | 2.2 | 13 | 0 | m.i. | 1.259 | 30.8 | 56 | 6 | m.i. | 93 |
| HVC2 | | | 15.2 | 0.171 | 1.639 | 31.6 | 39 | 7 | 0 | 0.247 | 4.8 | 12 | 0 | m.i. | 1.867 | 36.3 | 51 | 7 | m.i. | 94 |
| HVR1 | | RDH | 7.8 | 0.155 | 0.705 | 29.3 | (67) | (11) | 0 | 0.067 | 2.8 | 19 | 1 | m.i. | 0.765 | 32.1 | (86) | (12) | m.i. | (130) |
| HVR2 | | | 13.4 | 0.172 | 1.400 | 30.3 | 41 | 6 | 0 | 0.228 | 4.9 | 13 | 0 | m.i. | 1.612 | 35.3 | 53 | 6 | m.i. | 95 |
| HVR3 | | | 22.9 | 0.167 | 1.445 | 18.9 | 40 | 6 | 0 | 0.829 | 10.8 | 11 | 0 | m.i. | 2.251 | 29.7 | 51 | 6 | m.i. | 87 |

**Notes:** 1. m.i. - Value could not be determined because of matrix interference.
2. Analytes present at concentrations below their detection limits were assumed to be present at a concentration of one-half of the detection limit.

**Table IV. Fate of Chlorine in Softwood Pulp Bleaching**

| | | Unbl. Pulp | | D0 Stage | | | | | | (EO) Stage | | | | | Total | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Yields of Cl Cpds, Mole % $ClO_2$ | | | | | Yields of Cl Cpds, Mole % $ClO_2$ | | | | | Yields of Cl Cpds, Mole % $ClO_2$ | | | | |
| Expt. | Process | Pulp Type | Kappa Number | Kappa Factor | AOX, kg/t | AOX | $Cl^-$ | $ClO_3^-$ | $ClO_2^-$ | AOX, kg/t | AOX | $Cl^-$ | $ClO_3^-$ | $ClO_2^-$ | AOX, kg/t | AOX | $Cl^-$ | $ClO_3^-$ | $ClO_2^-$ | Total Cl Recovery, % |
| SCC1 | Conv. | Conv. | 18.7 | 0.050 | 0.095 | 5.1 | (114) | 4 | 2 | 0.068 | 3.6 | (124) | 12 | 2 | 0.176 | 8.7 | (238) | 16 | 4 | (268) |
| SCC2 | | | | 0.200 | 0.656 | 8.8 | 74 | 18 | 1 | 0.176 | 2.4 | 15 | 3 | 1 | 0.772 | 11.1 | 89 | 21 | 2 | 123 |
| SCC3 | | | 30.4 | 0.200 | 1.300 | 10.7 | n.d. | n.d. | n.d. | 0.130 | 1.1 | n.d. | n.d. | n,d, | 1.43 | 11.8 | n.d | n.d | n.d. | n.d. |
| SCC4 | | | 33 | 0.200 | 1.210 | 9.2 | n.d. | n.d. | n.d. | 0.160 | 1.2 | n.d. | n.d. | n.d. | 1.37 | 10.4 | n.d. | n.d. | n.d. | n.d. |
| SVC1 | Vapor | | 30.7 | 0.050 | 0.297 | 9.6 | 75 | 2 | 1 | 0.216 | 7.0 | 19 | 0 | 1 | 0.476 | 16.6 | 94 | 2 | 2 | 115 |
| SVC2 | | | | 0.184 | 1.261 | 11.2 | 56 | 10 | 0 | 0.846 | 7.5 | 15 | 0 | 0 | 1.955 | 18.6 | 71 | 10 | 0 | 100 |

Notes: 1. n.d. - Not determined.
2. Analytes present at concentrations below their detection limits were assumed to be present at a concentration of one-half of the detection limit.

## CONCLUSIONS

Vapor phase $ClO_2$ delignification of hardwood kraft pulps made from sweetgum is remarkably more efficient than conventional, low consistency $ClO_2$ delignification. At 0.2 kappa factor, delignification efficiency in the $D_0$(EO) partial sequence, expressed as kappa number reduction per percent of active chlorine consumed, was 4.4-5.3 for the vapor phase $D_0$ stage, as compared to 3.0-3.9 for the low consistency $D_0$ stage.

In the case of southern pine kraft pulps, there was a much smaller improvement in delignification efficiency in going from low consistency to vapor phase bleaching. This observation differs from those made earlier by others, indicating that vapor phase delignification efficiency is sensitive to operating conditions.

Vapor phase delignification of hardwood kraft pulps generated abnormally large quantities of AOX under the conditions employed in this study, and conventional $ClO_2$ delignification of hardwood pulps generated more AOX than expected on the basis of softwood bleaching data. AOX yields in $D_0$(EO) delignification of hardwood pulps from the present study are 14% for a low consistency $D_0$ stage and 33% for a vapor phase $D_0$ stage. These figures may be compared with the 8% to be expected on the basis of earlier softwood pulp bleaching data.

Vapor phase filtrates contained somewhat lower concentrations of chloride ion, and a greater proportion of the chloride ion produced in the vapor phase process was released in the alkaline extraction stage. The vapor phase filtrates also contained markedly less chlorate ion. These observations, as well as the observations of improved delignification efficiency and higher AOX yields, are consistent with the hypothesis that $ClO_2$ partially decomposes in the vapor phase before reacting with the pulp.

Qualitatively similar observations were made in the vapor phase $D_0$(EO) delignification of softwood kraft pulps, but the trends were generally less pronounced than in the case of the hardwood pulps. Under the conditions used in this study, vapor phase delignification produced an AOX yield of approximately 18%, as compared to approximately 10% in conventional, low consistency $ClO_2$ delignification. Positive effects of increasing kappa factor on the yields of both AOX and chlorate ion were also observed.

Differences in the structure of residual lignin after conventional and vapor phase bleaching were slight. This may indicate that the superior bleaching efficiency of the vapor phase process is due to diminished importance of reactions that occur between active chlorine compounds and dissolved organic byproducts. The absence of such reactions would leave no evidence in the residual lignin structure. This explanation is also consistent with the elevated AOX levels resulting from vapor phase bleaching if it is assumed that part of the dissolved organic material that consumes active chlorine in the liquid phase is chlorine substituted.

## ACKNOWLEDGMENTS

Financial assistance of this research by the United States Department of Energy and by the Member Companies of the Institute of Paper Science and Technology is gratefully acknowledged. We thank Mr. C. Courchene for assistance with preparation of wood chips and pulps, and Dr. Jian Jiang and Mr. K. Crofut of Ahlstrom Machinery Corporation for providing some of the softwood kraft pulps. We also thank Mr. T. Runge for assistance with the softwood bleaching, and Mr. J. Sealey and Mr. F. Chakar for lignin isolation and structural analysis. Analysis of the bleaching filtrates by capillary ion electrophoresis was performed by Mr. M. Buchanan and Mr. D. Roth of the IPST Chemical Analysis Group.

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# APPENDIX II

# CHLORINE DIOXIDE BLEACHABILITY OF PINE KRAFT PULPS MADE WITH CONTROLLED LIQUOR CONCENTRATION PROFILES

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## ABSTRACT

In an effort to assign a cause for the superior bleachability of pulps made by modified pulping processes, we have conducted systematic bleaching studies of southern pine pulps prepared with two types of controlled liquor concentration profiles. In one type, the alkali concentration, after an initial decrease, was maintained at a constant value. In the second type, the same kind of alkali profile was augmented by continuous liquor replacement to limit the concentrations of dissolved lignin and other reaction products. Neither type of profiling had any effect on the bleachability of the resulting pulps in the $D_0(EO)D_1E_2D_2$ bleaching sequence. Structural analyses of residual lignins showed that alkali profiled cooks gave residual lignins having slightly lower contents of phenolic groups, both uncondensed and condensed, as well as lower contents of aliphatic hydroxyl groups. These differences may contribute to the failure of the pulps from the profiled cooks to exhibit better bleachability than those from conventional cooks

## INTRODUCTION

The chlorine dioxide bleachability of softwood pulps made by modified continuous kraft pulping processes is known to be superior to that of conventional kraft pulps having the same kappa number (1,2). Since, in modified kraft cooking, the time profiles of the concentrations of all pulping liquor components are different from the corresponding profiles in conventional cooks, it is not yet possible to associate the improved bleachability with particular liquor component concentrations. Consequently, we have conducted laboratory pulping experiments in which the alkali and lignin concentration profiles were altered in controlled ways, and have systematically studied the bleaching response of the resulting pulps. We have also isolated residual lignins from some of the pulps and have analyzed them by nuclear magnetic resonance to correlate lignin structural features with pulping conditions and bleaching response.

## EXPERIMENTAL

### Pulping

All pulping was carried out at Auburn University in an M/K Systems 6-liter laboratory digester, modified to accommodate NIR and conductivity sensors, and equipped for continuously injecting and/or removing liquor during the cook. All cooks were done according to the same temperature schedule, which incorporated a 40-minute rise from ambient temperature to a maximum cooking temperature of 170°C.

Two types of profiled cooks were conducted. Both were started by charging all of the sulfide required to give a time-averaged sulfidity of 30%, together with a fraction of the alkali corresponding to the desired total alkali charge level. In one type, the alkali concentration was allowed to fall from its initial value to some predetermined level, at which point alkali was added at a rate equal to the rate at which it was consumed, to maintain a constant concentration. The rate of addition was controlled by continuous, on-line measurement of lignin concentration by near infrared (NIR) spectroscopy. Duplicate cooks of this type were done to reach a kappa number target of 17 at each of two total effective alkali (EA) charge levels, 24% and 28% (as $Na_2O$, based on o.d. wood). Although these charge levels are somewhat higher than those found industrially, they corresponded to alkali concentrations typically found in commercial digesters because of the somewhat higher than normal liquor-to-wood ratio (5.5) used in our experiments. This was necessary because at any given time, a significant fraction of the pulping liquor was in the external circulation loop used for indirect heating and sensing of liquor component concentrations. During the constant alkali concentration period, the EA concentration was maintained at 14 g/L in the 24% EA cooks and 18 g/L in the 28% EA cooks. Figure 1 shows the EA and dissolved lignin (DL) profiles in a typical cook of this type.

In the second type of profiled cook, both the EA and DL concentration profiles were controlled. When the EA concentration had fallen to the desired value, alkali addition was begun to maintain that value, and was continued until the DL concentration had risen to the value at which it was to be controlled. At this point a black liquor bleed stream was initiated to control the DL concentration, while at the same time alkali was continuous ly fed to maintain the EA level constant. Figure 2 shows the EA and dissolved lignin (DL) profiles in a typical cook of this type.

All pulps were prepared at Auburn University, washed and shipped to the Institute of Paper Science and Technology, where they were screened, further characterized and bleached.

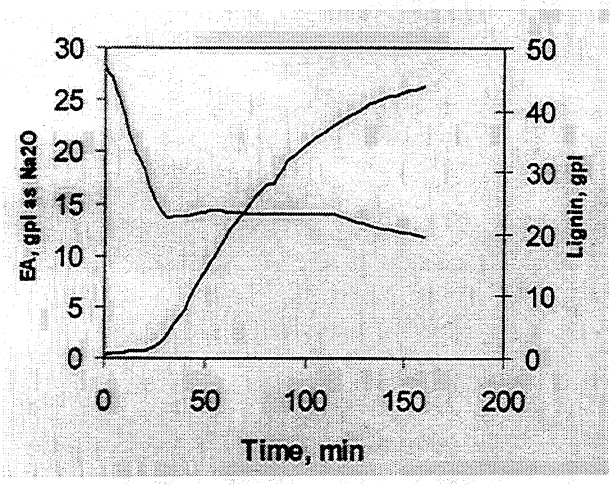


Figure 1. Effective alkali and dissolved lignin profiles in a Type 1 profiled cook. Feed liquor was exhausted at a time of 120 min.

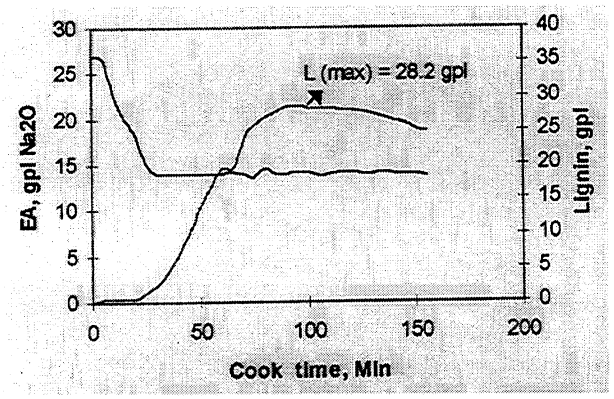


Figure 2. Effective alkali and dissolved lignin profiles in a Type 2 profiled cook.

### Bleaching

All bleaching employed the $D_0(EO)D_1E_2D_2$ sequence, each stage, except the $D_0$ and (EO) stages, being conducted at 10% consistency in sealed polyester bags. The first stage was carried out at kappa factor 0.20 for 30 min. at 45°C in a Quantum mixer. The (EO) stage was done at 70°C and 10% consistency in a horizontal shaft peg mixer rotating at 200 rpm, and lasted for 60 minutes. The oxygen pressure, initially at 60 psig., was decreased by 12 psig. every five minutes during the first 30 minutes, and the alkali charge was either 1.6% (16-18 kappa no. pulps) or 2.4% (30-34 kappa no. pulps). The $D_1$ and $D_2$ stages were conducted for 180 minutes at 70°C, and the $E_2$ stage was at 70°C for 60 minutes, with a NaOH charge of 0.4%.

After the (EO) stage, each pulp was divided into three equal portions, which were then bleached in the $D_1$ stage with 0.8, 1.2, and 1.6% $ClO_2$. Each of the resulting $D_1$ pulps was then extracted with caustic and further subdivided for bleaching with 0.2, 0.4 and 0.8% $ClO_2$ in the $D_2$ stage.

### Residual Lignin Isolation and NMR Analysis

The isolation of lignin from the kraft pulps was accomplished employing standard literature methods (3). In brief, air-dried pulp (60 g oven-dry weight) was added to an aqueous 0.1 N HCl (146 ml 1 N HCl), p-dioxane (1300 ml freshly distilled) solution, and this mixture was then refluxed for 2 hr. under an argon atmosphere. The mixture was then filtered, and the filtrate was filtered through celite. The solution was neutralized with sodium bicarbonate and concentrated under reduced pressure. After the filtrate was vacuum distilled to less than 10% of the original volume, water was added (3 x 200 mL) and the mixture was reconcentrated under reduced pressure. The aqueous solution was then acidified to pH 2.5 with an aqueous 1N HCl solution. The resulting precipitate was collected, washed several times with distilled water, and freeze-dried.

NMR data were acquired with a DMX 400 MHz Bruker spectrometer. Quantitative $^{31}$P-NMR experiments were performed following standard literature methods (4).

### Pulp Testing

Kappa number, viscosity and ISO brightness were determined according toTAPPI Test Methods.

## RESULTS AND DISCUSSION

### Unbleached Pulps

Table 1 shows the results obtained when the unbleached pulps were characterized. Alkali profiling resulted in significant viscosity increases, and solids profiling gave a slight increase in brightness. Decreasing the unbleached kappa number significantly increased brightness.

### $D_0(EO)$ Bleaching

Table 2 compares the $D_0(EO)$ response of pulps from alkali profiled and conventional kraft cooks at the two different EA concentration levels. It is apparent that, with the possible exception of a slight improvement in delignification efficiency, profiling had little effect on either the kappa number reduction or the brightness increase in the first two stages of the bleaching sequence.

Table 3 compares pulps from conventional and solids profiled (Type II) cooks with respect to their $D_0(EO)$

bleachability. Again, little difference was observed between the two types of cooks in this respect.

### $D_0(EO)D_1$ Bleaching

The pulps of Tables 2 and 3 were further bleached in a $D_1$ stage, by applying three different levels of $ClO_2$: 0.8, 1.2 and 1.6% (o.d. pulp basis). The end pH was 4.0, with a standard deviation of 0.4, and the residual $ClO_2$ ranged from 0.01% up to 0.36%, with the exception of two bleaches (out of a total of 36) in which only a trace of residual was found.

Table 1. Properties of unbleached pulps.

| Pulp Type[1] | Rep-licate | Kappa Number | Visc., mPa.s | Bright-ness |
|---|---|---|---|---|
| 24C | 1 | 16.3 | 16.9 | 28.6 |
| | 2 | 16.2 | 16.7 | 32.1 |
| 24AP | 1 | 17.3 | 22.9 | 29.2 |
| | 2 | 17.0 | 23.9 | 28.6 |
| 28C | 1 | 16.3 | 15.3 | 28.4 |
| | 2 | 16.3 | 13.6 | 31.1 |
| 28AP | 1 | 17.8 | 18.2 | 30.3 |
| | 2 | 17.3 | 16.7 | 28.4 |
| 20C | 1 | 31.9 | 32.5 | 25.6 |
| | 2 | 31.2 | 31.1 | 25.1 |
| 20AP | 1 | 34.1 | 39.5 | 24.8 |
| | 2 | 32.8 | 40.2 | 26.2 |
| 20SP | 1 | 33.6 | 46.0 | 26.1 |
| | 2 | 30.5 | 35.5 | 27.5 |

[1]First two digits indicate EA charge. Letter codes as follows: C - conventional control; AP - alkali profiled; SP - solids (dissolved lignin) profiled.

Table 2. $D_0(EO)$ bleaching of conventional and alkali profiled cooks.

| Unbleached Pulp | | | | $D_0(EO)$ Stage | | |
|---|---|---|---|---|---|---|
| EA | Cook Type | Kappa Number | Bright-ness | Delta Kappa /TAC | Bright-ness | Brtns. Gain |
| 24 | C | 16.3 | 28.6 | 4.0 | 52.1 | 24 |
| | | 16.2 | 32.1 | 4.0 | 50.9 | 19 |
| 24 | AP | 17.3 | 29.2 | 4.0 | 50.6 | 21 |
| | | 17.0 | 28.6 | 4.1 | 52.5 | 24 |
| 28 | C | 16.3 | 28.4 | 3.9 | 52.4 | 24 |
| | | 16.3 | 31.1 | 3.9 | 53.0 | 22 |
| 28 | AP | 17.8 | 30.3 | 4.2 | 52.5 | 22 |
| | | 17.3 | 28.4 | 4.0 | 52.2 | 24 |

Table 3. $D_0(EO)$ bleaching of conventional and solids profiled cooks.

| Unbleached Pulp | | | | $D_0(EO)$ Stage | | |
|---|---|---|---|---|---|---|
| EA | Cook Type | Kappa Number | Bright-ness | Delta Kappa /TAC | Bright-ness | Brtns. Gain |
| 20 | C | 31.9 | 25.6 | 4.3 | 50.5 | 25 |
| | | 31.2 | 25.1 | 4.4 | 51.2 | 26 |
| 20 | SP | 33.6 | 26.1 | 4.3 | 50.2 | 24 |
| | | 30.5 | 27.5 | 4.4 | 54.5 | 27 |

For all pulps, plots of brightness vs. $ClO_2$ consumed assumed the same form and could be described by the equation (2):

$$y = b_0 + b_1 \cdot [\, 1 - \exp(-b_2 \cdot x)] \quad \text{..... (Equation 1)}$$

in which $y$ is the brightness after the stage and $x$ is the amount of $ClO_2$ consumed, as % of o.d. pulp. The equation describes a brightness that rises as the amount of $ClO_2$ consumed is increased, rapidly at first and at an increasingly slower rate as the brightness asymptotically approaches an upper limit, or "brightness ceiling." Fitting this equation to data obtained by bleaching a particular pulp sample provides values of the three parameters, $b_0$, $b_1$, and $b_2$, which collectively describe the bleachability of the sample. Thus, $b_0$ represents the brightness when no $ClO_2$ has been consumed, or the brightness of the pulp before bleaching; $b_1$ represents the maximum possible brightness gain; and $b_2$ indicates how rapidly the brightness ceiling is approached as the amount of $ClO_2$ consumed is increased, and may therefore be referred to as the *response factor*. Differentiation of the equation shows that the slope at $x$=0 is $b_1 b_2$, from which it is apparent that $b_2$ is the slope normalized by the maximum possible gain. For given values of $b_0$ and $b_1$, pulps having higher values of $b_2$ require less $ClO_2$ to reach any given brightness.

Table 4 gives the experimentally determined values of these parameters for $D_1$ stage bleaching of conventional and alkali profiled pulps at two different alkali levels.

Table 4. $D_1$ stage bleachability parameters for pulps from conventional and alkali profiled cooks.

| Unbleached Pulp | | | | $D_1$ Stage | |
|---|---|---|---|---|---|
| EA | Cook Type | Kappa Number | $D_0(EO)$ Bright-ness | Bright-ness Ceiling, $b_0+b_1$ | Re-sponse Factor, $b_2$ |
| 24 | C | 16.3 | 52 | 85.7 | 5.5 |
| | | 16.2 | 51 | 87.1 | 2.7 |
| 24 | AP | 17.3 | 51 | 86.4 | 3.2 |
| | | 17.0 | 53 | 87.2 | 3.2 |
| 28 | C | 16.3 | 52 | 87.7 | 3.4 |
| | | 16.3 | 53 | 87.7 | 3.2 |
| 28 | AP | 17.8 | 53 | 87.4 | 3.3 |
| | | 17.3 | 52 | 87.4 | 4.2 |

It may be concluded from these data there were no significant differences in either brightness ceiling or response factor in the $D_1$ stage attributable to alkali profiling.

The corresponding comparison of conventional and solids profiled (Type II) cooks is shown in Table 5. A slight increase in $D_1$ response factor, but no change in $D_1$ brightness ceiling, can be attributed to solids profiling.

Table 5. $D_1$ stage bleachability parameters for pulps from conventional and solids profiled cooks.

| Unbleached Pulp | | | $D_0$(EO) Bright-ness | $D_1$ Stage | |
|---|---|---|---|---|---|
| EA | Cook Type | Kappa Number | | Bright-ness Ceiling, $b_0+b_1$ | Re-sponse Factor, $b_2$ |
| 20 | C | 31.9 | 51 | 87.1 | 2.7 |
| | | 31.2 | 51 | 88.8 | 2.1 |
| 20 | SP | 33.6 | 50 | 87.4 | 2.8 |
| | | 30.5 | 55 | 87.3 | 3.0 |

### $D_0(EO)D_1E_2D_2$ Bleaching

Each of the 36 pulps represented by the entries in Tables 4 and 5 were alkali extracted and further bleached in a $D_2$ stage, by applying three different levels of $ClO_2$: 0.2, 0.4 and 0.8% (o.d. pulp basis). In each case, nonlinear regression analysis of the resulting brightness response curve was used to determine the parameters in equation 1. The values of $b_2$ could not be satisfactorily estimated because the lowest $ClO_2$ charge used, 0.2%, gave a brightness increase that was so large as to make the initial slope of the curve difficult to discern. On the other hand, the brightness ceiling, ($b_0$ + $b_1$), could be estimated with good precision, and is plotted in Figures 3-5. The $D_2$ stage brightness ceiling is dependent on the level of $ClO_2$ used earlier in the sequence, and is accordingly plotted as a function of the $ClO_2$ charge in the $D_1$ stage.

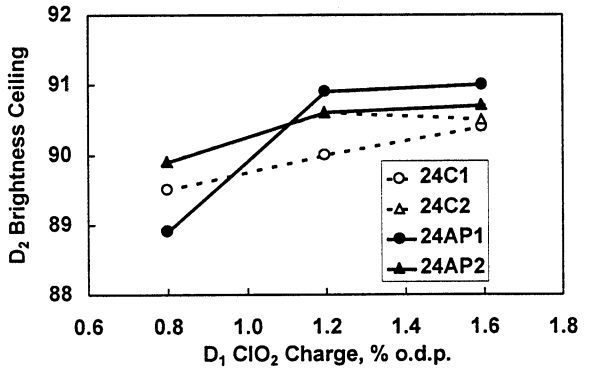


Figure 3. Final brightness ceiling for pulps from conventional (24C1 and 24C2) and Type I alkali profiled (24AP1 and 24 AP2) cooks with 24% EA.

Figure 3 shows no statistically significant difference between the brightness ceilings for pulps from conventional and alkali-profiled cooks at the 24% EA level. A similar conclusion can be drawn from Figure 4, which shows no significant difference between the corresponding pulps prepared with 28% EA.

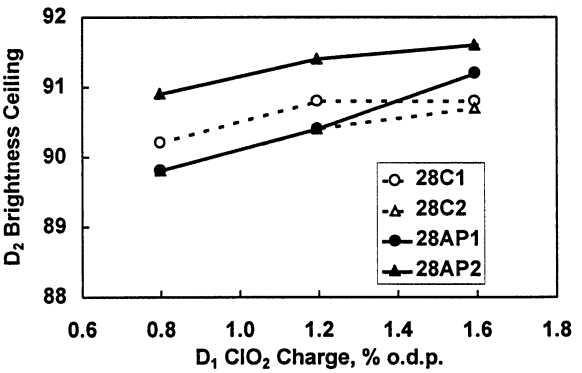


Figure 4. Final brightness ceiling for pulps from conventional (28C1 and 28C2) and Type I alkali profiled (28AP1 and 28 AP2) cooks with 28% EA.

Figure 5 compares the brightness ceilings of pulps prepared with and without profiling of both EA and DL, as shown in Figure 2. Again, no statistically significant difference was observed between the conventional and profiled pulps.

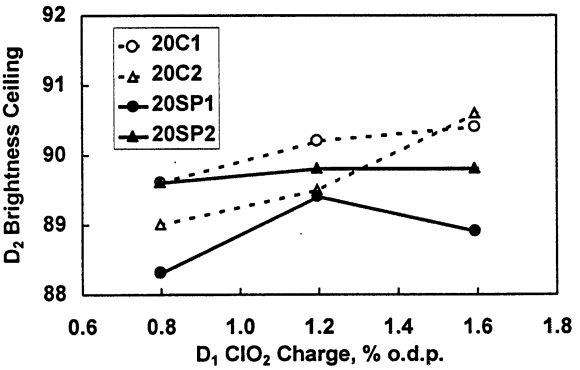


Figure 5. Final brightness ceiling for pulps from conventional (20C1 and 20C2) and Type 2 alkali and dissolved lignin profiled (20SP1 and 20 SP2) cooks with 20% EA.

### Residual Lignin Structure

Table 6 contains the results of analyses of residual lignins isolated from pulps prepared by conventional and profiled cooks with 24% EA. The data suggest that

the alkali profiled cooks gave residual lignins having slightly lower contents of phenolic groups, both uncondensed and condensed, as well as lower contents of aliphatic hydroxyl groups. The former difference is consistent with an earlier observation that phenolic content alone can not be used to predict bleachability (5).

The lower content of aliphatic hydroxyl groups may suggest that elimination of sidechain γ-carbons as formaldehyde occurred to a greater extent in the profiled cooks. This, in turn, suggests a greater degree of accompanying enol ether formation, which might be expected to adversely affect bleachability. This, together with the lower phenolic content, may contribute to the failure of the pulps from the profiled cooks to exhibit better bleachability than those from the conventional cooks. These negative effects must be balanced by a compensating positive effect of liquor profiling, which remains unidentified, and which may account for the observation that pulps from modified cooking processes are somewhat more easily bleachable than conventional pulps. It appears possible that the positive effect is related to a higher content of surviving ether linkages in pulps from modified cooks (5).

Table 6. Structural features of lignins isolated from pulps prepared in conventional and alkali-profiled cooks.

| EA | Cook Type | Kappa Number | Acids | Guaiacyl & Demeth. PhOH | 5-Substituted Guaiacyl | Aliphatic Hydroxy |
|---|---|---|---|---|---|---|
| 24 | C | 16.3 | 0.22 | 1.06 | 0.62 | 1.16 |
| | | 16.2 | 0.33 | 1.07 | 0.59 | 1.05 |
| 24 | AP | 17.3 | 0.28 | 0.94 | 0.54 | 0.95 |
| | | 17.0 | 0.18 | 0.88 | 0.53 | 0.73 |

## CONCLUSIONS

Controlling alkali profiles during kraft cooking of southern pine under the conditions used in this study had no significant effect on the bleachability of the resulting pulps at an unbleached kappa number of 16-18. The conditions prevailing during the profiled cooks were as follows: 24-28% EA, 5.5:1 liquor-to-wood ratio, temperature increased from ambient to a maximum temperature of 170 °C during the period from t=0 to t=40 min., 30 % sulfidity, all sulfide added at beginning of cook, initial EA concentration 28 g/L, falling linearly to 14 g/L from t=0 to t=30 min., maintained at 14 g/L from t=30 to t=115 min., and then falling linearly to 12 g/L at t=160 min., at which point the cook was terminated. In the same cook, the concentration of dissolved lignin increased from 0 at t=0 to 44 g/L at t=160 min.

A lower content of aliphatic hydroxyl groups in pulps from profiled cooks may suggest a greater degree of enol ether formation which, together with a lower phenolic content, may contribute to the failure of the pulps from the profiled cooks to exhibit better bleachability than those from conventional cooks.

Controlling both alkali and dissolved solids profiles under the conditions used in this study had no significant effect on the bleachability of the resulting pulps at an unbleached kappa number of 31-34. The conditions prevailing during the profiled cooks were as follows: 20% EA, 5.5:1 liquor-to-wood ratio, temperature increased from ambient to a maximum temperature of 170 °C from t=0 to t=40 min., 30 % sulfidity, all sulfide added at beginning of cook, initial EA concentration 28 g/L, falling linearly to 14 g/L from t=0 to t=30 min., and maintained at 14 g/L fromt=30 to t=155 min., at which point the cook was terminated. In the same cook, the concentration of dissolved lignin increased from 0 at the beginning of the cook to 28 g/L at t=90 min, after which it fell approximately linearly to 26 g/L at t=155 min.

Any beneficial effect of modified cooking on bleachability must be attributed to effects not simulated in our profiling experiments to date.

## ACKNOWLEDGMENTS

Financial assistance of this research by the United States Department of Energy, the Member Companies of the Auburn University Pulp and Paper Industrial Advisory Committee, and the Member Companies of the Institute of Paper Science and Technology is gratefully acknowledged. We thank Miss Michelle Alger for assistance with the bleaching experiments.

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# APPENDIX III

# Effects of Washer Efficiency on Characteristics of Effluents from D(EPO)D Bleaching of a Softwood Kraft Pulp

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## ABSTRACT

This paper describes the results of a systematic study of AOX, BOD, and COD released by bleaching southern pine kraft pulp in the $D_0(EPO)D_1$ sequence at a kappa factor of 0.20 and a $D_1$ stage $ClO_2$ charge of 1.2%. Measurements of all three parameters were made at three different levels of carryover of $D_0$ stage filtrate into the (EPO) stage and three different levels of carryover of (EPO) stage effluent into the $D_1$ stage, and the entire experiment was duplicated.

The combined AOX contributions of the $D_0$ and (EPO) stages amounted to 11.6% of the chlorine atoms applied in the $D_0$ stage, while the contribution of the $D_1$ stage amounted to 2.7% of the chlorine atoms applied in the $D_1$ stage. The combined AOX contributions of all three stages decreased when the $D_0$ stage carryover was increased from 0 to 10% and was unaffected by (EPO) stage carryover. With perfect washing between stages, COD contributions to the combined bleach plant filtrates by the $D_0$, (EPO) and $D_1$ stages were, respectively, 14.1, 39.8, and 2.9 kg/odumt. The combined COD contributions of all three stages was relatively unaffected by a low level (5%) of $D_0$ stage carryover, but a higher level (10%) resulted in an overall COD increase of 2 kg/odumt. Increasing (EPO) stage carryover from 0 to 30% decreased total COD by 3 kg/t. With perfect washing between stages, BOD contributions to the combined bleach plant filtrates by the $D_0$, (EPO), and $D_1$ stages were, respectively, 3.8, 7.0, and 2.2 kg/odumt. No significant effect of carryover levels on the total BOD release could be detected.

## INTRODUCTION

Kraft pulp bleaching sequences that do not make use of molecular chlorine are rapidly becoming the norm throughout the world, and are virtually mandated in the United States by the Environmental Protection Agency's "Cluster Rules."[1] One important sequence type relies on chlorine dioxide, $ClO_2$, to accomplish both bulk delignification in the first stage and brightening in the latter stages. Detailed knowledge of the environmentally relevant characteristics of the effluents these sequences generate is needed to allow them to be evaluated for specific applications.

The characteristics of the filtrates from individual stages are of less interest than those of the entire bleach plant effluent that results when the filtrates from all stages are combined before being sent to the effluent treatment system. Because the byproducts of any bleaching stage are subject to possible destruction in a subsequent stage, it is reasonable to expect that the characteristics of the combined effluent may be determined not only by the products of the reactions between the bleaching chemical and pulp components in each stage, but also by the proportion of these products that are carried with the pulp into the following stage, as opposed to being discharged directly to the sewer. Consequently, it is of interest to determine the effect of bleach plant washer efficiency on effluent characteristics, and important to recognize it in laboratory evaluations of bleaching sequences from an effluent quality standpoint.

In the present study, we determined properties of individual stage and combined filtrates from laboratory bleaching of a southern pine kraft pulp in the D(EPO)D sequence.

## EXPERIMENTAL

### Pulping

Southern pine chips from a southeastern U.S. coastal mill were screened and pulped in a 2.0 $ft^3$ batch digester heated indirectly with steam. The following conditions were used: effective alkali (% o.d. wood): 16; sulfidity (%): 25; maximum temperature (°C): 170; liquor-to-wood ratio (L/kg): 4:1; H-factor: 2058; chip charge (g.o.d.): 6000.

The pulp was disintegrated and screened on a 0.010" slotted flat screen. The Kappa number of the screened pulp was 26.

**Bleaching**

$D_0$ stages were performed on 100-g (o.d. basis) samples in a Quantum Technologies high-shear mixer at a kappa factor of 0.20 for 30 minutes at 45°C and 4% consistency. The pulp was preheated in a microwave oven, and its pH was adjusted with $H_2SO_4$ before adding the $ClO_2$, to achieve a final pH of 2.0. After $ClO_2$ addition, the pulp was mixed for 7 seconds and for 7 seconds every 3 minutes thereafter. At the end of the retention period, the filtrate was sampled for pH and residual measurement.

The pulp was transferred to a funnel and filtered to remove as much full-strength filtrate as possible. The filtrate was set aside for use as carryover or for analysis. (The filtrates were stored overnight at 4°C at the pH of the stage.) The pulp was then washed twice by dilution to 3% consistency followed by vigorous mixing and filtering.

The extraction stage was carried out in an agitated pressurized reactor at 70°C and 10% consistency for 60 minutes. The NaOH charge was 3.2% when no $D_0$ filtrate was present and was otherwise adjusted to give an exit pH between 11.0 and 11.4. The charge of $H_2O_2$ was 0.5%, and the reactor was pressurized with oxygen at 60 psig. initially. At intervals of 10 min., the oxygen pressure was decreased to 50, 40, and 0 psig. The pulp, NaOH, and carryover (when applied) were first mixed and heated in a microwave oven before being placed in the reactor. The peroxide was added while the pulp was in the reactor. At the end of the stage, the pulp was sampled, filtered, and washed as described above.

The $D_1$ stage was carried out in polyester bags in a controlled water bath at 70°C. The $ClO_2$ charge was 1.2%. The pulp, dilution water, and NaOH or $H_2SO_4$ were first mixed together and put in the bag. Then the chlorine dioxide was added and the bag sealed. After mixing by hand, the bag was carefully opened to measure the pH. Then it was sealed again, heated in the microwave oven, and placed in the water bath until the color of the filtrate indicated that only a trace of residual remained. The pulp was filtered and washed and the filtrate was collected as described above. Exit pH, $ClO_2$ residual, and ISO brightness were measured.

**Filtrate Preparation and Analysis**

The individual stage filtrates were collected and refrigerated until the sequence was complete. Typically, there was a delay of one day between collection of the $D_0$(EOP) and $D_1$ effluents. A sample of combined filtrate was prepared using individual filtrates in the proportions: $D_0$:(EOP):$D_1$= 24(1-c1) : 9(1-c2) : 9, where c1 = (% carryover from stage 1)/100 and c2 = (% carryover from stage 2)/100.

Filtrate samples for AOX analysis were treated with $Na_2S_2O_3$, pH-adjusted to < 2 with concentrated $HNO_3$ and stored at 4°C. Filtrate samples for COD were pH-adjusted to < 2 with 4N $H_2SO_4$ and stored at 4 °C. Samples for BOD analysis were adjusted to pH 7.0 with NaOH or $H_2SO_4$. Immediately after collection and pH adjustment, the samples were refrigerated and shipped in insulated containers.. Testing was completed within 48 hours of collection..

All filtrate tests were done by Savannah Laboratories, Mobile, AL, according to the following methods: AOX-EPA Method 1650 rev. B[2], COD-Standard method 5220C[3], and BOD-Standard method 5210[3].

**Experimental Design and Analysis**

The experimental design was a replicated $3^2$ factorial with a doubly replicated center point. It encompassed 20 independent runs, each starting with a different sample of unbleached pulp. The two variables investigated were the fraction of the total $D_0$ stage filtrate carried with the pulp into the (EPO) stage (0, 5, and 10%) and the fraction of the total (EPO) filtrate carried into the $D_1$ stage (0, 15, and 30%). The resulting data were analyzed by multiple regression, for which purpose the variables were coded, to simplify the equations. The variable XD was defined such that its values were, respectively, -1, 0, and +1 when the $D_0$ stage carryover levels were 0, 5, and 10%. The variable XE was defined such that its values were, respectively, -1, 0, and +1 when the (EPO) stage carryover levels were 0, 15, and 30%. Objective statistical techniques were used to identify outlying observations, which were discarded before doing the regression analysis. Outliers are shown within parentheses in the data tables. The regression model used included the terms XD, XE, $XD^2$, $XE^2$, and XD·XE. Only those terms significant at a confidence level of 95% or greater were retained.

## RESULTS AND DISCUSSION

Pulp properties and residual chemical levels are shown in Table 1. In all cases, only a trace of residual $ClO_2$ remained at the end of the 30-min $D_0$ stage retention time. Similarly, no more than a trace of residual $H_2O_2$ was found at the end of the (EPO) stage.

The concentrations of AOX, COD, and BOD in individual stage filtrates and total and combined discharge rates are shown in Tables 2-4.

### Bleaching Efficiency

As Table I shows, the levels of $D_0$ stage carryover employed had no significant effect on the (EPO) kappa number, although a barely discernible (93% confidence) adverse effect on brightness was noted. The 95% confidence interval for the mean kappa number after the (EPO) stage was 3.60 ± 0.07. The (EPO) brightness decreased from 63.7 with perfect washing after the $D_0$ stage to 63.0 at the 10% carryover level. As described below, however, $D_0$ stage carryover had no effect on final brightness.

**Table I Experimental Bleaching Data**

| | | (EPO) Stage | | $D_1$ Stage | | | |
|---|---|---|---|---|---|---|---|
| % $D_0$ Filtrate Carryover | % (EPO) Filtrate Carryover | Kappa No. | Bright-ness | Exit pH | $ClO_2$ Residual, % o.d.p. | $ClO_2$ Con-sumed, % o.d.p. | Bright-ness |
| 0 | 0 | 3.8 | 63.1 | 4.00 | 0.039 | 1.16 | 87.3 |
| | | 3.6 | 64.1 | 4.20 | 0.039 | 1.16 | 87.2 |
| | 15 | 3.5 | 64.1 | 4.35 | 0.058 | 1.14 | 87.4 |
| | | 3.5 | 64.2 | 4.60 | 0.078 | 1.12 | 87.1 |
| | 30 | 3.7 | 63.3 | 4.50 | 0.037 | 1.16 | 85.5 |
| | | 3.7 | 62.9 | 4.80 | 0.073 | 1.13 | 85.2 |
| 5 | 0 | 3.5 | 63.8 | 4.95 | 0.136 | 1.06 | 87.9 |
| | | 3.8 | 63.4 | 4.70 | 0.107 | 1.09 | 87.2 |
| | 15 | 3.5 | 64.3 | 4.30 | 0.058 | 1.14 | 86.8 |
| | | 3.7 | 62.4 | 4.10 | 0.029 | 1.17 | 86.7 |
| | | 3.5 | 64.2 | 4.00 | 0.044 | 1.16 | 87.0 |
| | | 3.8 | 63.8 | 4.50 | 0.092 | 1.11 | 87.2 |
| | 30 | 3.6 | 62.4 | 4.55 | 0.068 | 1.13 | 86.4 |
| | | 3.6 | 63.4 | 4.85 | 0.102 | 1.10 | 85.3 |
| 10 | 0 | 3.7 | 63.5 | 4.30 | 0.058 | 1.14 | 87.8 |
| | | 3.3 | 63.1 | 4.30 | 0.054 | 1.15 | 87.4 |
| | 15 | 3.4 | 63.0 | 4.50 | 0.068 | 1.13 | 86.4 |
| | | 3.6 | 62.9 | 4.35 | 0.073 | 1.13 | 87.1 |
| | 30 | 3.7 | 62.9 | 4.75 | 0.083 | 1.12 | 85.9 |
| | | 3.6 | 62.3 | 4.85 | 0.088 | 1.11 | 85.1 |

Although we attempted to control the $D_1$ stage exit pH at 4.5, it varied between 4 and 5, with some effect on the amount of residual $ClO_2$ that remained at the end of the $D_1$ stage. Regression analysis of the residual $ClO_2$ data gave the following equation:

$$\text{Res. } ClO_2 = 0.1(pH) - 0.014(XE) - 0.013(XE)^2 - 0.38,$$

which gives the residual as a percentage of o.d. pulp weight, and for which the multiple correlation coefficient, $R^2$, and the standard error of estimate, s, were, respectively, 0.85 and 0.011.

This equation shows that a pH increase from 4.0 to 5.0 increases the residual $ClO_2$ by 0.1% (o.d. pulp basis). The pH did not, however, affect the brightness obtained. The above equation also shows that, at constant $D_1$ stage exit pH, increasing (EPO) stage carryover from 0 to 15% has no effect on the residual $ClO_2$ level, but a further increase from 15 to 30% causes the residual to decrease by 0.03% (o.d. pulp basis).

A corresponding regression analysis of final brightness showed a similar dependence on carryover level, but no dependence on pH. The following equation was obtained:

$$\text{Brightness} = 87.0 - 1.0(XE) - 0.5(XE)^2,$$

for which $R^2$ and s were, respectively, 0.89 and 0.31. This equation shows that increasing (EPO) stage carryover from 0 to 15% decreases final brightness by 0.5 point, while a further increase from 15 to 30% causes a further brightness decrease of 1.5 points. The overall effect of carrying over 30% of the (EPO) stage filtrate into the $D_1$ stage is thus a 2-point loss in bleached brightness.

### AOX

Table II contains the results of determinations of AOX in each of the individual stage filtrates and combined effluent samples. These are expressed both as observed concentrations in mg/L and releases calculated on a pulp weight basis by taking into account the consistency of the stage and the fraction of the filtrate released to the sewer rather than being carried over to the next stage.

The concentration of AOX found in the $D_0$ stage filtrate is expected to be the same for all experiments, since the experimental variables did not affect $D_0$ stage conditions. After rejection of a single outlying observation, the mean AOX concentration was 39.9 mg/L, and the standard deviation was 5.4. The 95% confidence interval for the mean is 39.9 ± 2.6 mg/L, corresponding to a formation rate of 0.96 ± 0.06 kg/odumt (oven-dry unbleached metric ton). This corresponds to conversion of (9.2 ± 0.6)% of the applied chlorine atoms to AOX.

**Table II Observed AOX Concentrations and Discharges**

| % $D_0$ Effluent Carryover | % (EPO) Effluent Carryover | Found in Effluent, mg/L | | | Discharged, kg/ODUMT | |
|---|---|---|---|---|---|---|
| | | $D_0$ Stage | (EPO) Stage | $D_1$ Stage | Total of Stage Contributions | Combined Effluent |
| 0 | 0 | 43 | 30 | 17 | 1.46 | 1.34 |
| | | 41 | 35 | (38) | 1.64 | 1.68 |
| | 15 | 47 | 25 | 23 | 1.53 | 1.38 |
| | | 49 | 25 | 23 | 1.57 | 1.46 |
| | 30 | 34 | 35 | 29 | 1.30 | 1.26 |
| | | 42 | 29 | 43 | 1.58 | 1.49 |
| 5 | 0 | 40 | 21 | 24 | 1.32 | 1.35 |
| | | 34 | 26 | 20 | 1.19 | 1.35 |
| | 15 | (21) | (15) | 17 | (0.75) | (0.75) |
| | | 47 | 32 | 33 | 1.61 | 1.70 |
| | | 41 | 21 | 23 | 1.30 | 1.30 |
| | | 37 | 23 | 20 | 1.20 | 1.62 |
| | 30 | 41 | 29 | 34 | 1.42 | 1.33 |
| | | 29 | (16) | 27 | 1.01 | 1.10 |
| 10 | 0 | 37 | 30 | 11 | 1.17 | 1.27 |
| | | 43 | 30 | 13 | 1.32 | 1.62 |
| | 15 | 40 | 24 | 33 | 1.34 | 1.34 |
| | | 35 | 24 | 23 | 1.15 | 1.15 |
| | 30 | 33 | 31 | 31 | 1.19 | 1.44 |
| | | 46 | 37 | 43 | 1.61 | 1.25 |

The average concentration of AOX found in the (EPO) stage filtrate, after eliminating two suspiciously low values, was 28.2 mg/L, with a standard deviation of 4.8 mg/L. There was no significant effect of $D_0$ carryover level on the concentration of AOX in the (EPO) filtrate, suggesting that AOX carried into this stage is destroyed. Studies by Cook[4] on the Ultim-O process have also shown that a significant portion of the AOX is destroyed in the extraction stage. The 95% confidence interval for the mean AOX concentration was 28.2 ± 2.4 mg/L, corresponding to a formation rate of 0.25 ± 0.02 kilograms per oven-dry unbleached metric ton (kg/odumt). The total rate of formation in the first two stages was therefore 1.21 kg/odumt, which corresponds to conversion of 11.6% of the applied chlorine atoms to AOX. This value is somewhat lower than the value of 13.6% calculated from a model based on an analysis of literature data obtained by bleaching with $ClO_2$-rich mixtures of $ClO_2$ and $Cl_2$.[5] The difference may reflect differences between pure $ClO_2$ and mixtures.

The concentration of AOX in the $D_1$ filtrates increased when the level of carryover from the (EPO) stage was increased. The following regression equation was obtained:

$$D_1 \text{ AOX, mg/L} = 26.2 + 7.0(XE)$$

for which $R^2$ and s were, respectively, 0.37 and 7.4. Despite the relatively low $R^2$, the effect of carryover was significant at the 99.5% confidence level. This is consistent with the expectation that AOX carried into a $D_1$ stage will not be destroyed in that stage. Furthermore, comparison of the coefficient for XE in the above equation with the concentration of AOX in the (EPO) filtrate suggests that additional AOX is formed in the $D_1$ stage from material in the carryover from the (EPO) stage. An increase in (EPO) stage carryover from 0 to 30% corresponds to an increase in XE of two units (from -1 to +1), for which the above equation predicts an increase of 14 mg/L or 0.13 kg/odumt. The (EPO) filtrate entering this stage contained only 30% of 0.25 or 0.08 kg/odumt.

From a practical viewpoint, the amount of AOX discharged to the treatment system per ton of pulp is of more interest than its concentration in the filtrates from individual stages. The amount of AOX released from a given stage is the amount formed, less the amount carried with the pulp into the next stage, except for the last stage in the sequence, which is assumed to release all of the AOX present in the filtrate emerging with the pulp from the bleaching tower. All of these releases are then combined, and the amount of AOX discharged from the pulp mill to the treatment system is their sum, less any loss that occurs as a result of chemical reaction after mixing. Table II contains the individual stage releases, their sums, and the total discharge calculated from the AOX concentration in the combined effluent. The latter two figures will be the same, in the absence of experimental error, unless some AOX is destroyed or created by chemical reaction after mixing of the individual stage filtrates.

Regression analysis of the sum of the individual stage releases ("Total AOX"), after rejection of one outlying observation, gave the following equation:

$$\text{Total AOX, kg/odumt} = 1.36 - 0.11(XD)$$

for which $R^2$ and s were, respectively, 0.22 and 0.17. This equation reflects the earlier observations that $D_0$ AOX is destroyed in the (EPO) stage, but that (EPO) AOX is unaffected by the $D_1$ stage. The low $R^2$ value reflects the fact that the effect of $D_0$ stage carryover is small in comparison to the total discharge, but the carryover effect is nevertheless significant at the 95% confidence level.

The Total AOX discussed above was next compared to the total discharge calculated from the AOX concentration in the combined effluent by means of a paired t-test. The two figures may be expected to differ to the extent that AOX is destroyed or created upon mixing of the filtrates from individual stages. The t-test showed that there was no significant difference between them. The 95% confidence interval for the difference was 0.03±0.08 kg/odumt (0.01±0.06 if the three largest differences were discarded). This result, together with the observed effect on the total AOX, leads to the conclusion that increasing $D_0$ stage carryover decreased overall AOX release. It also shows that there was negligible loss of AOX due to chemical reaction upon mixing acid and alkaline effluents. This conclusion, however, should be viewed in light of the fact that the effluents were combined under laboratory conditions (low temperature and near-neutral pH) that did not favor chemical reaction. This would not be true in the mill, and mill experience suggests that AOX destruction does occur as a result of mixing the effluents from the individual bleaching stages.[5]

## COD

Table III contains the results of determinations of COD in each of the individual stage filtrates and combined effluent samples, expressed both as observed concentrations in mg/L and releases in kg/odumt.

**Table III Observed COD Concentrations and Discharges**

| % $D_0$ Effluent Carryover | % (EPO) Effluent Carryover | Found in Effluent, mg/L | | | Discharged, kg/ODUMT | |
|---|---|---|---|---|---|---|
| | | $D_0$ Stage | (EPO) Stage | $D_1$ Stage | Total of Stage Contribu-tions | Combined Effluent |
| 0 | 0 | 590 | 4500 | 350 | 57.8 | 58.8 |
| | | 540 | (5000) | (1000) | (67.0) | 58.8 |
| | 15 | 610 | (5100) | (910) | (61.8) | 52.8 |
| | | 630 | 4400 | 780 | 55.8 | 52.8 |
| | 30 | 580 | 4300 | 1300 | 52.7 | 55.0 |
| | | 600 | 4500 | 1400 | 55.4 | 55.0 |
| 5 | 0 | 590 | 4400 | 250 | 55.3 | 53.0 |
| | | 560 | 4400 | 350 | 55.5 | 53.0 |
| | 15 | 600 | 4500 | 760 | 54.9 | 51.3 |
| | | 610 | 4500 | 800 | 55.5 | 51.3 |
| | | 590 | 4300 | 740 | 53.0 | 51.3 |
| | | 580 | 4500 | 780 | 54.7 | 55.2 |
| | 30 | 590 | 4400 | 1400 | 53.8 | 53.3 |
| | | 620 | 4400 | 1300 | 53.6 | 53.3 |
| 10 | 0 | 580 | 4900 | 380 | 60.0 | 59.4 |
| | | 610 | 4900 | 280 | 59.8 | 55.4 |
| | 15 | 580 | 5000 | 800 | 58.0 | 53.6 |
| | | 550 | 4900 | 760 | 56.2 | 61.2 |
| | 30 | (660) | 4800 | 1400 | 57.1 | 59.0 |
| | | 570 | 4900 | 1500 | 56.7 | 55.4 |

The concentration of COD in the $D_0$ stage filtrate is unaffected by bleach plant washer inefficiency. Its average value, after discarding one outlying observation, was 588 mg/L and its standard deviation was 23 mg/L. The 95% confidence interval for the mean was 588±11 mg/L, corresponding to a formation rate of 14.1±0.3 kg/odumt.

Regression analysis of the (EPO) stage COD concentration data gave an equation that was significantly nonlinear with respect to $D_0$ stage carryover. It suggested that there was no effect of carrying over 5% of the $D_0$ stage effluent, but that when the $D_0$ carryover level was increased to 10% there was a significant increase in (EPO) filtrate COD concentration. When two outlying observations were discarded and the regression analysis was repeated, the conclusion was the same. This analysis gave the equation:

$$\text{(EPO) COD, mg/L} = 4425 + 238(XD) + 238(XD)^2$$

for which $R^2$ and s were, respectively, 0.92 and 74. Substitution in this equation predicts COD concentrations of 4425, 4425, and 4900 at $D_0$ carryover levels of 0, 5, and 10%, respectively. Converting these to a pulp weight basis gives 39.8, 39.8 and 44.1 kg/odumt, respectively. By contrast, the expected values, based on the rate of COD formation in the $D_0$ stage, are 39.8, 40.5, and 41.2 kg/odumt. The discrepancy at the high carryover level suggests that amounts of $D_0$ carryover that exceed a threshold limit may effectively catalyze COD formation in the (EPO) stage, for example, by destroying peroxide or inhibiting oxidation.

The concentration of COD in the $D_1$ filtrates increased at an increasing rate when the level of carryover from the (EPO) stage was increased. After discarding two outliers, the following regression equation was obtained:

$$D_1 \text{ COD, mg/L} = 774 + 531(XE) + 78(XE)^2$$

for which $R^2$ and s were, respectively, 0.99 and 54. Substitution in the above equation predicts COD concentrations of 322, 774, and 1383 mg/L at (EPO) carryover levels of 0, 15, and 30%, respectively. Converting these to a pulp weight basis gives 2.9, 7.0, and 12.4 kg/odumt. The expected values, based on the average COD concentration in the (EPO) filtrate, are 2.9, 9.1, and 15.3 kg/odumt. The comparison suggests that COD in the carryover is partially destroyed in the $D_1$ stage, and that proportionally more is destroyed when the carryover level is lower.

The amounts of COD released per ton of pulp are also shown in Table III. Regression analysis of the total of the individual stage COD releases, after discarding two outliers identified earlier, gave the following equation:

$$\text{Total COD, kg/odumt} = 54.5 + 1.1(XD) - 1.4(XE) + 2.3(XD)^2$$

for which $R^2$ and s were, respectively, 0.83 and 1.0. This equation predicts that total COD will be relatively unaffected by low levels (~5%) of $D_0$ stage carryover, but that a higher level (~10%) will result in an overall COD increase of 2 kg/odumt. It also predicts that increasing (EPO) stage carryover from 0 to 30% will decrease total COD by 3 kg/t. The former effect is indicative of a detrimental effect of $D_0$ carryover on (EPO) COD, and the latter to partial destruction of (EPO) COD in the $D_1$ stage.

The Total COD discussed above was next compared with the total discharge calculated from the COD concentration in the combined effluent by means of a paired t-test. The two figures may be expected to differ to the extent that COD is destroyed or created upon mixing of the filtrates from individual stages. After discarding the results for the two outliers, the t-test showed that there was no significant difference between them. The 95% confidence interval for the difference (Total - Combined) was 1.0 ± 1.3 kg/odumt. This result, together with the observed effect on the total COD, leads to the conclusion that increasing $D_0$ stage carryover increases overall COD discharge, while increasing (EPO) carryover decreases it.

## BOD

Measurement of BOD concentration in the single-stage filtrates and combined effluents gave the data shown in Table IV.

Analysis of the $D_0$ filtrate BOD data was complicated by the observation that their distribution was skewed to the right. This departure from normality was corrected by first taking their reciprocals, which were normally distributed. The resulting 95% confidence interval for the mean BOD concentration in the $D_0$ filtrate was 159 ± 15 mg/L, corresponding to a formation rate of 3.82 ± 0.36 kg/odumt.

The (EPO) stage filtrate BOD's showed no significant dependence on $D_0$ carryover level. The 95% confidence interval for the mean (EPO) stage filtrate BOD was 778 ± 52 mg/L, corresponding to a formation rate of 7.00 ± 0.47 kg/odumt. Either $D_0$ BOD carryover was destroyed in the (EPO) stage or the precision of the BOD determinations was not good enough to detect the small difference (0.2-0.4 kg/odumt) expected.

The concentratiom of BOD in the $D_1$ filtrate increased with increasing (EPO) stage carryover, as described by the regression equation:

$$D_1 \text{ BOD, mg/L} = 336 + 87\,(XE)$$

for which $R^2$ was 0.48 and s was 74. Substitution in the above equation predicts BOD concentrations of 249, 336 and 423 mg/L at (EPO) carryover levels of 0, 15, and 30%, respectively. Converting these to a pulp weight basis gives 2.2, 3.0, and 3.8 kg/odumt. The expected values, based on the average BOD concentration in the (EPO) filtrate, are 2.2, 3.2, and 4.3 kg/odumt. The comparison indicates that roughly 20% of the BOD in the carryover is destroyed in the $D_1$ stage.

The amounts of BOD released per ton of pulp are also shown in Table IV. Regression analysis of the total of the individual stage BOD releases showed no significant effect of the carryover levels on the total BOD release. Failure to detect effects corresponding to the observed effects on COD could be due either to their absence or to the fact that the precision of the BOD measurements, relative to their mean, is poorer than in the case of COD. After deletion of one outlier, calculation of a 95% confidence interval for the total BOD release was 12.54 ± 0.65 kg/odumt.

**Table IV Observed BOD Concentrations and Discharges**

| % $D_0$ Effluent Carryover | % (EPO) Effluent Carryover | Found in Effluent, mg/L | | | Discharged, kg/ODUMT | |
|---|---|---|---|---|---|---|
| | | $D_0$ Stage | (EPO) Stage | $D_1$ Stage | Total of Stage Contribu-tions | Combined Effluent |
| 0 | 0 | 190 | 670 | 290 | 13.20 | 13.44 |
| | | 140 | 720 | 280 | 12.36 | 11.34 |
| | 15 | 130 | 1000 | 270 | 13.20 | 11.79 |
| | | 180 | 750 | 470 | 14.29 | (15.04) |
| | 30 | 150 | 670 | 470 | 12.05 | 12.58 |
| | | 130 | 730 | 300 | 10.42 | 11.79 |
| 5 | 0 | 140 | 730 | 220 | 11.74 | (4.49) |
| | | 250 | 860 | 300 | (16.14) | 12.65 |
| | 15 | 140 | 940 | 330 | 13.35 | 12.23 |
| | | 150 | 610 | 240 | 10.25 | 10.26 |
| | | 160 | 930 | 390 | 14.27 | 11.05 |
| | | 130 | 660 | 320 | 10.89 | 11.84 |
| | 30 | 130 | 690 | 450 | 11.36 | 9.91 |
| | | 150 | 940 | 340 | 12.40 | 12.95 |
| 10 | 0 | 130 | 820 | 220 | 12.17 | 13.07 |
| | | 140 | 730 | 200 | 11.39 | (16.63) |
| | 15 | 230 | 810 | 230 | 13.23 | 10.33 |
| | | 250 | 690 | 400 | 14.28 | 10.71 |
| | 30 | 170 | 750 | 460 | 12.54 | 11.44 |
| | | 220 | 850 | 530 | 14.88 | 11.44 |

An independent estimate of the total BOD discharge was obtained by analyzing combined filtrate samples and converting the resulting concentrations to mass-based discharges. After elimination of three outlier, these data were also subjected to regression analysis. As in the case of the total of the single-stage releases discussed above, no significant effects of the carryover levels were detected. After elimination of three outliers, the 95% confidence interval for the combined BOD discharge was calculated to be 11.69 ± 0.54 kg/odumt.

The two estimates of total BOD discharge were compared by a paired t-test, after excluding the four cases in which either estimate was an outlying observation. The result indicated that the total BOD in the combined filtrates was slightly less than the sum of the contributions of all of the single-stage filtrates, the 95% confidence interval for the difference being 0.92 ± 0.89 kg/odumt, or about 7% of the sum of the contributions of the individual stages.

## CONCLUSIONS

From this study of $D_0(EPO)D_1$ bleaching of southern pine kraft pulp at 0.20 kappa factor and a $ClO_2$ charge of 1.2% in the $D_1$ stage, with $D_0$ stage carryover levels ranging from 0 to 10% and (EPO) stage carryover levels ranging from 0 to 30%, the following conclusions may be drawn.

### Bleaching Efficiency

1. $D_0$ stage carryover, at a level of 10%, has no significant effect on the (EPO) kappa number.
2. Increasing (EPO) stage carryover from 0 to 15% decreases final brightness by 0.5 point, while a further increase from 15 to 30% causes a further brightness decrease of 1.5 points. The overall effect of carrying over 30% of the (EPO) stage filtrate into the $D_1$ stage is thus a 2-point loss in bleached brightness.

### AOX

1. With perfect washing between stages, AOX contributions to the combined bleach plant filtrates by the $D_0$, (EPO), and $D_1$ stages are predicted to be, respectively, 0.96, 0.25 and 0.17 kilograms per oven-dry unbleached metric ton (kg/odumt). The combined contributions of the $D_0$ and (EPO) stages amount to 11.6% of the chlorine atoms applied in the $D_0$ stage, while the contribution of the $D_1$ stage amounts to 2.7% of the chlorine atoms applied in the $D_1$ stage.
2. Our failure to detect any significant effect of $D_0$ carryover level on the concentration of AOX in the (EPO) filtrate suggests that AOX carried into this stage is destroyed. AOX carried into a $D_1$ stage will not be destroyed in that stage. Furthermore, a small additional amount of AOX may be formed in the $D_1$ stage from material in the carryover from the (EPO) stage.

3. The combined AOX contributions of all three stages decreases by 0.22 kg/odumt when $D_0$ stage carryover is increased from 0 to 10% and is unaffected by (EPO) stage carryover.

**COD**

1. With perfect washing between stages, COD contributions to the combined bleach plant filtrates by the $D_0$, (EPO), and $D_1$ stages are predicted to be, respectively, 14.1, 39.8, and 2.9 kg/odumt.
2. Increasing $D_0$ stage carryover beyond 5% causes a larger-than-expected increase in (EPO) stage COD, suggesting that amounts of $D_0$ carryover that exceed a threshold limit may effectively catalyze COD formation in the (EPO) stage, for example, by destroying peroxide or inhibiting oxidation.
3. As (EPO) carryover is increased, there is a slightly smaller-than-expected increase in $D_1$ stage COD, suggesting that COD in the carryover is partially destroyed in the $D_1$ stage.
4. The combined COD contributions of all three stages is relatively unaffected by low levels (~5%) of $D_0$ stage carryover, but a higher level (~10%) results in an overall COD increase of 2 kg/odumt. Increasing (EPO) stage carryover from 0 to 30% will decrease total COD by 3 kg/t.

**BOD**

1. With perfect washing between stages, BOD contributions to the combined bleach plant filtrates by the $D_0$, (EPO), and $D_1$ stages are predicted to be, respectively, 3.8, 7.0, and 2.2 kg/odumt.
2. The (EPO) stage BOD shows no significant dependence on $D_0$ carryover level.
3. Although $D_1$ filtrate BOD increases with increasing (EPO) stage carryover, roughly 20% of the BOD in the carryover is destroyed in the $D_1$ stage.
4. No significant effect of the carryover levels on the total BOD release could be detected either because they were absent or because the precision of the BOD measurements, relative to their mean, is poorer than in the case of COD.
5. The total BOD in the combined filtrates was 11.7 kg/odumt, which was slightly less than the sum of the contributions of all of the single-stage filtrates (12.5 kg/odumt).

## ACKNOWLEDGMENTS

We gratefully acknowledge financial support of this research by the Georgia Consortium for Technological Competitiveness in Pulp and Paper and the Member Companies of the Institute of Paper Science and Technology.

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# APPENDIX IV

# Effective Alkali and Pulping Temperature Effects on the Bleachability of Birch and Maple Kraft Pulps

**Nidhi Rawat and Thomas J. McDonough**

## Introduction

The objective of this work was to study the effect of individual pulping variables on the ECF bleachability of hardwood kraft pulps at constant kappa number. This was done so that a comparison could be made between differently prepared pulps having roughly the same starting lignin content to gain insight into how and to what extent the bleachability of the pulps is affected by individual pulping variables. The two hardwood species that we chose to study were Maple and Birch.

Earlier work on Southern Pines conclusively demonstrated that the bleachability of kraft pulps can be affected by changing the pulping conditions. For Pine, emphasis was on effective alkali charge (EA) , because of indications in the literature that it has an effect. A more extensive experimental approach was adopted for hardwoods. Apart from EA, we also decided to study the effect of cooking temperature on the ECF bleachability of the pulps at a constant unbleached kappa number.

## Results and Discussion

### *Effect of EA on Birch and Maple Kappa Number at Increasing H-factor*

Series of microdigester cooks were performed to find approximate pulping conditions for preparing pulps at constant unbleached kappa number for bleachability studies. Both Maple and Birch kraft cooks were performed at three distinct EA levels of 12%,16% and 20% (as $Na_2O$) at constant sulfidity of 25%, L/W ratio 4:1 and 90 minutes ramp to the cooking temperature of 170°C.Pulp yield, screen rejects and kappa number were determined for all cooks and black liquors analyzed for residual alkali. The microcook results are recorded in Tables1-4.

Figures1 and 2 illustrate a well known relationship between H-factor and Kappa number for Maple and Birch pulps as a function of EA. We know that at constant temperature, the duration of pulping directly relates to the so called H-factor, a combined measure of time and temperature of the process. A lower target kappa number obviously requires a higher H-factor. However, the micro cook results showed that increasing the H-factor does not always decrease the kappa number. This is evident from the experimental data of Maple cook at low EA of 12 % and very high H-factor of 3200. The increase in kappa number on prolonging the cook reflects reprecipitation of dissolved lignin onto the fibers. This very undesirable phenomenon occurs when there is very little or no free alkali left in the pulping matrix to keep the reaction in the forward direction. Similar observations have been reported earlier for S. Pine pulping at low EA levels.

Further, these results also indicate that irrespective of EA, the rate of lignin removal is appreciably decreased at an H-Factor of 800 and more even though there is sufficient alkali in the spent liquor in some of the cases. Any effort to obtain low kappa number in the digester is accompanied by undesirable carbohydrate degradation vis-a-vis low strength properties of the resultant pulps.

### *Preparation of Pulps for Bleachability studies (M/K Digester cooks)*

The microdigester cook results led to the conditions that produced pulps for bleachability work and are listed in Tables 5 and 6. To study the EA effect, two pulps each from Maple and Birch of ~20 Kappa number were prepared at 14% and 20% EA (as Na2O ) at 170°C.For Pulping temperature effect on bleachability, pulps of ~20 kappa number were prepared at two pulping temperatures - 150° C and 180° C and 17% EA(as Na2O ) All the other pulping conditions were maintained constant as in the micro cooks. Results indicate that for Maple, pulping at high EA is a very attractive option since it significantly reduces the cooking time and produces brighter pulp at practically comparable pulp yield and viscosity.

Birch seems to be very sensitive to EA and pulping temperature increase, more so to EA increase. Pulping of Birch with high EA produces brighter pulp but of low yield and viscosity .

Increasing the pulping temperature from 150°C to 180°C negatively affected Birch yield and brightness whereas no such affect was observed for Maple.

### *Response in Do(EO) Partial Sequence*

As shown in Table 7 , the brightness after (EO) was higher for high EA pulps. The reason for this is that these pulps are characterized by higher unbleached pulp brightness. For Maple, increasing EA greatly reduces specific chemical consumption.

It is evident from Table 8 that, in the case of Birch, EA and Pulping temperature have no affect on specific chemical consumption in the Do and (EO) stages. It is also observed that high temperature pulping slightly impairs the short sequence bleachability of Birch but contrary is true for Maple.

### *Response in Do(EO)D1*

In the D1 stage pulps were bleached with 0.4% , 0.8% and 1.2% ClO2. Bleaching in the D1 stage revealed that high EA pulps in general were easily bleachable as shown in Figure 3.At any given ClO2 charge in D1 stage, the brightness difference between low and high EA pulps was as much as 5 points. Most importantly, increasing EA and pulping temperature resulted in Maple pulps which could be bleached to very high brightness of +90% ISO in only 3 stages i.e. Do(EO)D .A practical implication of this would be shortening of regular bleaching sequence from 5-stage to 3-stage with additional benefits in energy and bleaching chemicals savings.

On the other hand, Pulping temperature has opposite but comparatively less effect on both Maple and Birch pulp bleachability, as can be observed from Figure 4.

### *Response in Do(EO)DED*

In the D2 stage, the pulps were bleached with 0.2%, 0.4% and 0.8% ClO2.In the final analysis, final pulp brightness was plotted as a function of total ClO2 consumed in full sequence. Figure 5 shows that for both Maple and Birch, high EA pulps exhibit higher brightness for any given amount of ClO2 consumed or in other words high EA pulps consumes less ClO2 to achieve any target brightness.

Figure 6 illustrates the effect of Pulping temperature on the $ClO_2$ consumed to achieve a target brightness in ECF bleaching. For Birch, the negative effect of high temperature pulping on brightness disappears with increasing amount of $ClO_2$ in the final D2 stage of bleaching. High temperature pulps have a better bleaching response and produce pulps of higher brightness at low levels of $ClO_2$ consumption. However, the low temperature pulps could also be bleached to high brightness with increasing amount of $ClO_2$ charge.

A comparison between the hardwood species shows that Maple pulps have better bleachability than Birch and of the two pulping variables investigated, EA has a more pronounced effect on bleachability.

## Summary and Conclusions

The results of these initial studies indicate that the individual pulping variables i.e. EA and pulping temperature seem to affect the nature and bleachability of the pulp produced, to large or smaller extent. A very important outcome of this work was that High EA and high temperature pulping emerged as a very attractive option for Maple. High EA pulping significantly reduces the cooking time and produces brighter pulps at practically comparable pulp yield and viscosity. It also greatly enhances Maple pulp bleachability by producing very high brightness pulps in only 3 stages of ECF bleaching. That is to say a potential to increase in production throughput of the digester without any negative effect on pulp properties .

For Birch, high EA has a negative effect on pulp yield and viscosity although it greatly improves the bleaching response in ECF bleaching sequence. However, high temperature is somewhat better for Birch in a

way that it produces high brightness pulps with less $ClO_2$ consumption with insignificant effect on pulp yield and viscosity.

## Table1 : Micro Digester Pulping of Maple

| | EA | H- Factor 200 | 400 | 800 | 1600 | 3200 | Control (800) 1 | 2 | 3 |
|---|---|---|---|---|---|---|---|---|---|
| **Unsc. Pulp Yield , %** | **12%** | **54.6** | **53.7** | **52.8** | **51.8** | **52.1** | | | |
| **Sc. Pulp Yield , %** | | **7.6** | **46.9** | **52.6** | **51.8** | **52.1** | | | |
| **Kappa No.** | | **72.6** | **39.1** | **32.2** | **14.3** | **16.2** | | | |
| Date of Cook | | 10-Apr | 15-Apr | 22-Apr | 22-Apr | 15-Apr | | | |
| **Unsc. Pulp Yield , %** | **16%** | **59.8** | **48.7** | **48.7** | **47.4** | **40.2** | **48.4** | 50.6 | 49.3 |
| **Sc. Pulp Yield , %** | | **13.4** | **48.7** | **48.7** | **47.4** | **40.2** | **48.4** | 50.6 | 49.3 |
| **Kappa No.** | | **62** | **15.4** | **10.9** | **10.5** | **8.8** | **10.9** | 11.5 | 12.9 |
| Date of Cook | | 22-Apr | 10-Apr | 15-Apr | 22-Apr | 15-Apr | 10-Apr | 15-Apr | 22-Apr |
| **Unsc. Pulp Yield , %** | **20%** | **52.7** | **47.7** | **46.4** | **44.1** | **42.5** | | | |
| **Sc. Pulp Yield , %** | | **51.5** | **47.7** | **46.4** | **44.1** | **42.5** | | | |
| **Kappa No.** | | **21.7** | **11.2** | **8.2** | **6.9** | **6.1** | | | |
| Date of Cook | | 15-Apr | 22-Apr | 10-Apr | 15-Apr | 15-Apr | | | |

## Table2 : Micro Digester Pulping of Birch

| | EA | H- Factor 200 | 400 | 800 | 1600 | Control | ( 800 ) |
|---|---|---|---|---|---|---|---|
| **Unsc. Pulp Yield , %** | **12%** | **58.0** | **54.0** | **54.5** | **50.3** | | |
| **Sc. Pulp Yield , %** | | **13.0** | **31.0** | **54.3** | **50.3** | | |
| **Kappa No.** | | **75.5** | **42.3** | **22.7** | **15.5** | | |
| Date of Cook | | 15-May | 29-Apr | 29-Apr | 15-May | | |
| **Unsc. Pulp Yield , %** | **16%** | **54.4** | **50.9** | **48.1** | **48** | **48.5** | **47.4** |
| **Sc. Pulp Yield , %** | | **13.6** | **50.9** | **48.1** | **48.0** | **48.0** | **47.4** |
| **Kappa No.** | | **65.5** | **20.0** | **13.6** | **10.5** | **12.7** | **12.1** |
| Date of Cook | | 29-Apr | 29-Apr | 15-May | 15-May | 29-Apr | 15-May |
| **Unsc. Pulp Yield , %** | **20%** | **49.2** | **45.8** | **44.4** | **45.2** | | |
| **Sc. Pulp Yield , %** | | **20.4** | **45.8** | **44.4** | **45.2** | | |
| **Kappa No.** | | **50.1** | **9.9** | **9.0** | **8.7** | | |
| Date of Cook | | 29-Apr | 29-Apr | 15-May | 15-May | | |

## Table 3 : Micro Digester Pulping of Maple

| Black Liquor | EA | H- Factor 200 | 400 | 800 | 1600 | 3200 | Control ( 800 ) 1 | 2 | 3 |
|---|---|---|---|---|---|---|---|---|---|
| pH | 12% | 13.2 | 13.2 | 12.6 | 12.2 | 11.6 | | | |
| Na2S ,gpl as Na2O | | 5.6 | 5.3 | 4.8 | 4.7 | 1.4 | | | |
| NaOH , gpl as Na2O | | 6.8 | 5.7 | 4.1 | 3.8 | 3.9 | | | |
| Date of Cook | | 10-Apr | 15-Apr | 22-Apr | 22-Apr | 15-Apr | | | |
| pH | 16% | 13.4 | 13.4 | 13.4 | 13.4 | 13.4 | 13.4 | 13.4 | 13.4 |
| Na2S ,gpl as Na2O | | 7.4 | 7.2 | 6.0 | 5.9 | 3.6 | 7.5 | 5.9 | 6.7 |
| NaOH , gpl as Na2O | | 13.2 | 10.9 | 9.5 | 9.3 | 7.4 | 8.7 | 10.3 | 10.5 |
| Date of Cook | | 22-Apr | 10-Apr | 15-Apr | 22-Apr | 15-Apr | 10-Apr | 15-Apr | 22-Apr |
| pH | 20% | 13.8 | 13.8 | 13.8 | 13.8 | 13.4 | | | |
| Na2S ,gpl as Na2O | | 6.3 | 5.4 | 9.2 | 7.7 | 6.7 | | | |
| NaOH , gpl as Na2O | | 13.7 | 21.2 | 14.5 | 14.6 | 12.4 | | | |
| Date of Cook | | 15-Apr | 22-Apr | 10-Apr | 15-Apr | 15-Apr | | | |

## Table 4 : Micro Digester Pulping of Birch

| Black Liquor | EA | H- Factor 200 | 400 | 800 | 1600 | Control (800) 1 | 2 |
|---|---|---|---|---|---|---|---|
| pH | 12% | 13.4 | 12.8 | 12.6 | 12.2 | | |
| Na2S ,gpl as Na2O | | 15.1 | 5.3 | 4.7 | 4.2 | | |
| NaOH , gpl as Na2O | | 15.6 | 3.6 | 3.4 | 3.3 | | |
| Date of Cook | | 15-May | 29-Apr | 29-Apr | 15-May | | |
| pH | 16% | 13.4 | 13.2 | 13.2 | 13.1 | 13.4 | 13 |
| Na2S ,gpl as Na2O | | 8.3 | 6.0 | 7.0 | 7.5 | 8.8 | 7.0 |
| NaOH , gpl as Na2O | | 11.7 | 10.5 | 9.1 | 9.1 | 17.8 | 7.8 |
| Date of Cook | | 29-Apr | 29-Apr | 15-May | 15-May | 29-Apr | 15-May |
| pH | 20% | 13.4 | 13.2 | 13.2 | 13.2 | | |
| Na2S ,gpl as Na2O | | 7.1 | 7.3 | 10.1 | 8.2 | | |
| NaOH , gpl as Na2O | | 9.1 | 15.6 | 16.3 | 12.7 | | |
| Date of Cook | | 29-Apr | 29-Apr | 15-May | 515/1997 | | |

## Table 5: M/K Digester Pulping Of Hardwood Pulps

| Hard Wood | Birch | | Maple | |
|---|---|---|---|---|
| EA , % | 14 | 20 | 14 | 20 |
| H-Factor | 879.6 | 283.7 | 635.7 | 257.1 |
| Kappa Number | 19.4 | 18.7 | 20.4 | 20.3 |
| Total Yield ,% | 51.9 | 50.5 | 51.3 | 51.9 |
| Screened Yield , % | 49.3 | 44.8 | 49.8 | 50.8 |
| Brightness ,ISO | 30.2 | 36.7 | 34.8 | 43.5 |
| Viscosity | 71.8 | 48.7 | 41.6 | 41.5 |
| Black Liquor : | | | | |
| pH | 13.2 | 13.6 | 13.2 | 13.6 |
| NaOH , gpl as Na2O | 8.59 | 10.37 | 8.84 | 22.7 |
| Na2S , gpl as Na2O | 3.54 | 2.02 | 1.12 | 8.84 |
| StraightTitration to pH11 | 5.48 | 7.94 | 4.5 | 23.9 |
| NaOH , gpl as Na2O | | | | |

Cnstant Conditions :

Sulfidity , % = 25.0
Wood : Liquor ratio = 1:4
Pulping Temp. C = 170

## Table 6 : M/K Digester Pulping Of Hardwood Pulps

| Hard Wood | Birch | | Maple | |
|---|---|---|---|---|
| Pulping temp. C | 180 | 150 | 180 | 150 |
| EA , % | 17.0 | 17.0 | 17.0 | 17.0 |
| H-Factor | 582.2 | 646.1 | 578.8 | 607.6 |
| Kappa Number | 17.8 | 18.0 | 15.0 | 15.5 |
| Total Yield ,% | 47.5 | 49.2 | 51.0 | 50.9 |
| Screened Yield , % | 47.2 | 49.2 | 50.8 | 50.9 |
| Brightness ,ISO | 33.7 | 35.9 | 43.7 | 41.5 |
| Viscosity | 40.7 | 39.9 | 32.8 | 39 |
| Black Liquor : | | | | |
| pH | <14 | <14 | <14 | <14 |
| NaOH , gpl as Na2O | 13.4 | 14.1 | nd | nd |
| Na2S , gpl as Na2O | 7.2 | 7.7 | nd | nd |
| StraightTitration to pH11 NaOH , gpl as Na2O | 13.2 | 13.2 | 14.0 | 13.3 |

Cnstant Conditions :

Sulfidity , % = 25.0

Wood : Liquor ratio = 1:4

## Table 7 :Do(EO) Bleachability Parameters for Low and High EA Kraft Pulps

| Unbleached Pulp | | | Do | | E(O) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Type | H-F | Kappa | Exit pH | TAC | Exit pH | Kappa | TAC/dk | Bright. | Bright. Gain |
| **Birch LEA** | **880** | **19.4** | **1.8** | **3.88** | **11.3** | **4.6** | **0.26** | **58.9** | **28.7** |
| **Birch HEA** | **284** | **18.7** | **2.2** | **3.74** | **11.6** | **4.6** | **0.27** | **65.3** | **28.6** |
| **Maple LEA** | **636** | **20.4** | **2.3** | **4.08** | **11.2** | **4.4** | **0.26** | **66.3** | **31.5** |
| **Maple HEA** | **257** | **20.3** | **2.1** | **4.06** | **11.5** | **2.8** | **0.23** | **74.9** | **31.4** |

Bleaching Conditions :
Do Stage : 30 min. , 45 deg.C , 10% conty , Quantum reactor
E(O) Stage : 60 min. , 70 deg.C , 10 % conty , 1.6% NaOH o.d.p.

## Table 8:Do(EO) Bleachability Parameters for Hardwood Kraft Pulps at two Pulping Temperatures

| | Unbleached Pulp | | | Do | | E(O) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Type | H-F | Kappa | Exit pH | TAC | Exit pH | Kappa | TAC/dK | Bright. ‘ | Bright. Gain |
| Birch | LT | 646 | 18.0 | 1.8 | 3.56 | 11.5 | 4.5 | 0.27 | 65.6 | 29.7 |
| Birch | HT | 582 | 17.8 | 2.1 | 3.60 | 11.6 | 4.6 | 0.27 | 62.9 | 29.2 |
| Maple | LT | 608 | 15.5 | 2.1 | 3.10 | 11.7 | 3.9 | 0.27 | 71.4 | 29.9 |
| Maple | HT | 579 | 15.0 | 2.3 | 3.00 | 11.5 | 4.0 | 0.27 | 74.3 | 30.6 |

Bleaching Conditions :

Do Stage : 30 min. , 45 deg.C , 10% conty , Quantum reactor

E(O) Stage : 60 min. , 70 deg.C , 10 % conty , 1.6% NaOH o.d.p.

**Figure 1: Effect of Effective Alkali on Maple Kappa Number on Increasing H-Factor**

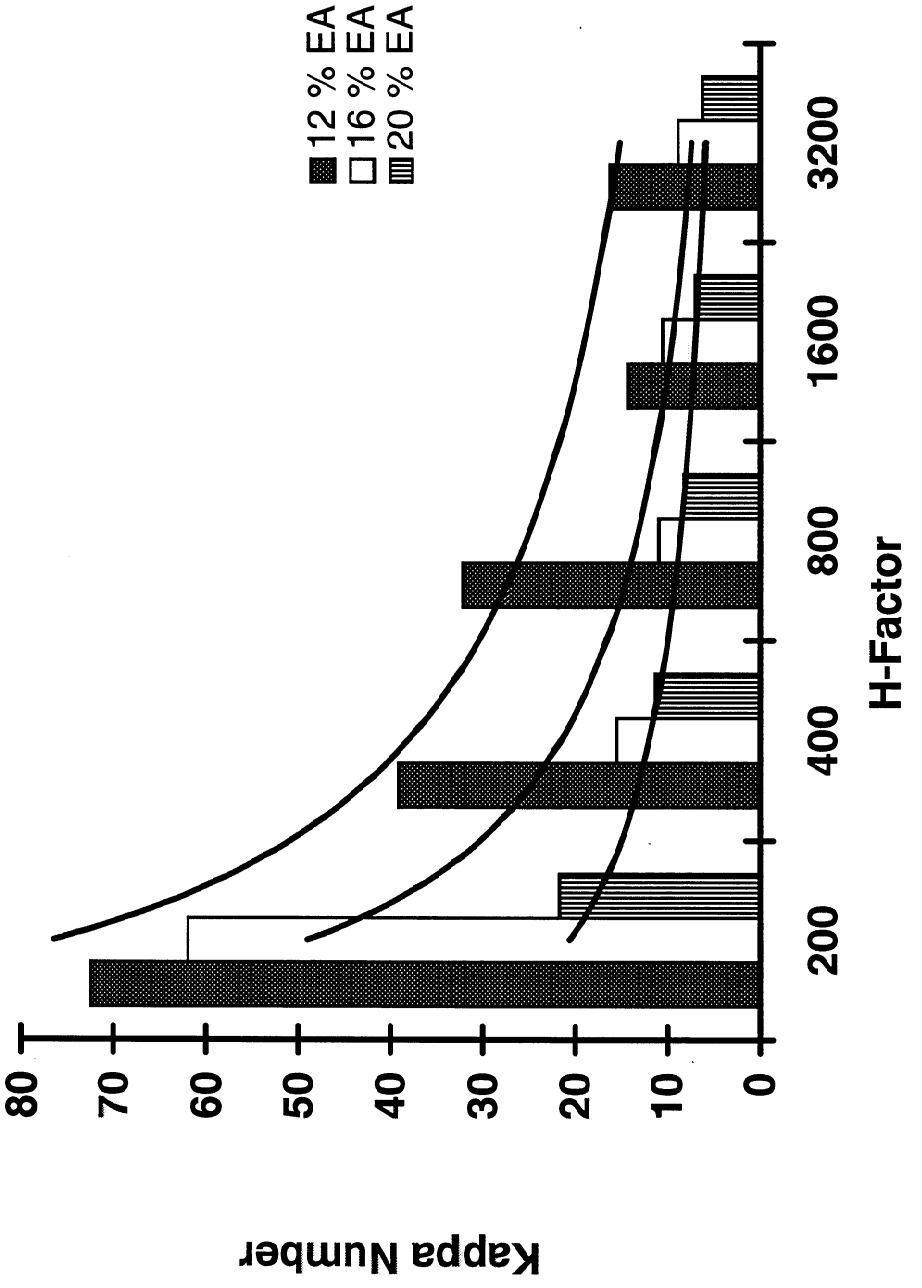
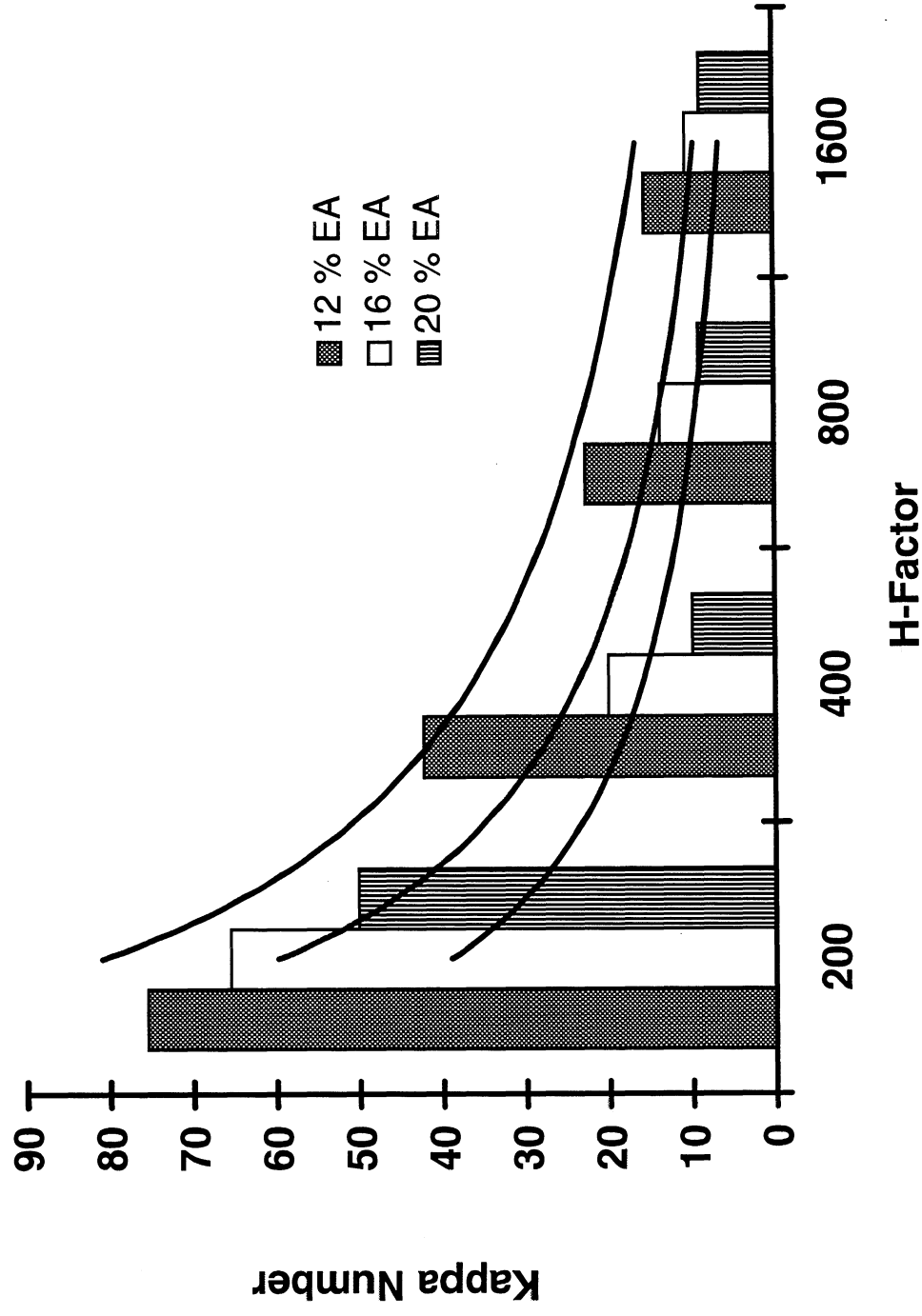
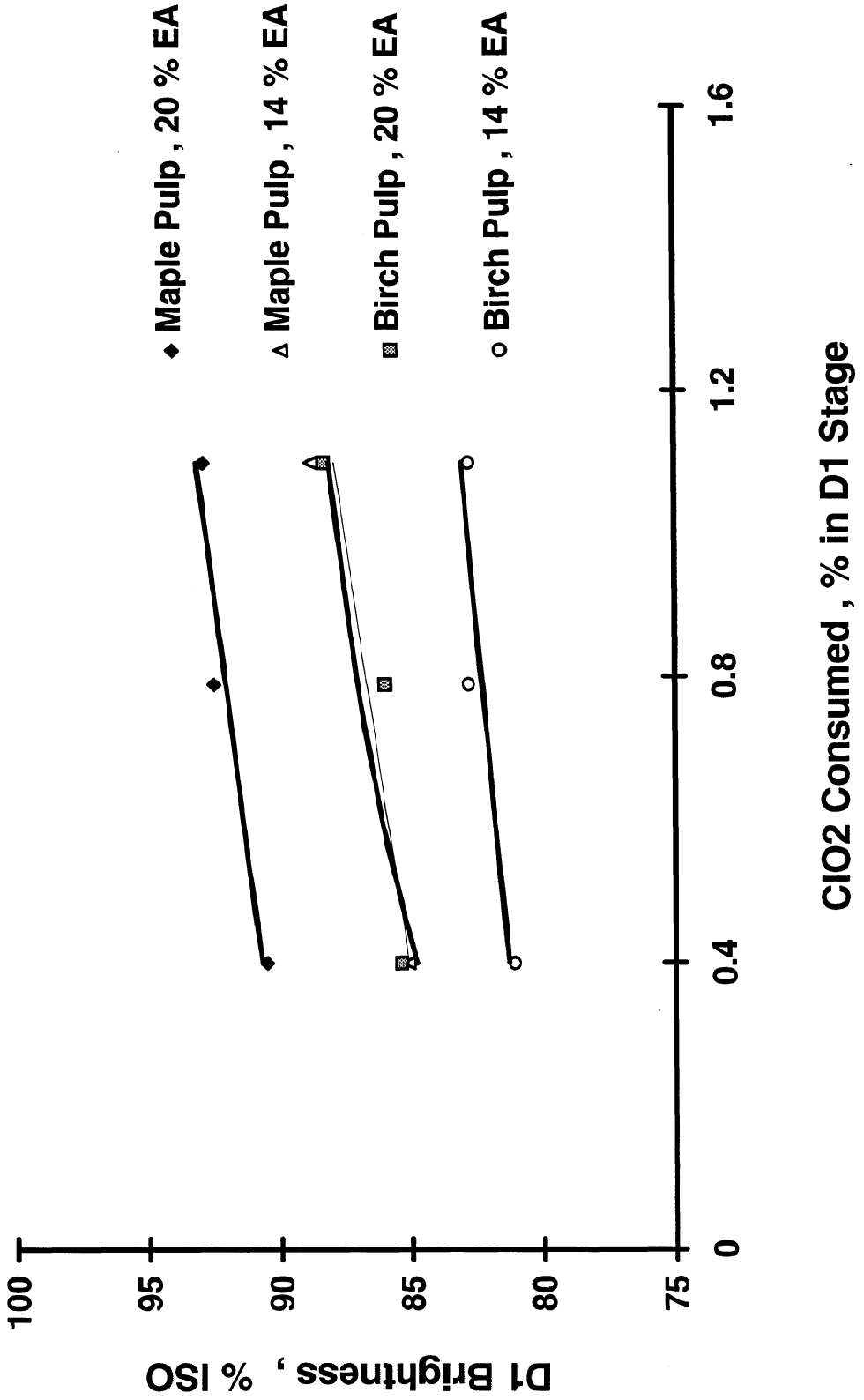


**Figure 2 : Effect of Effective Alkali on Birch Kappa Number on increasing H-Factor**



# Figure 3:Effect of Effective Alkali on D1 Stage Brightness



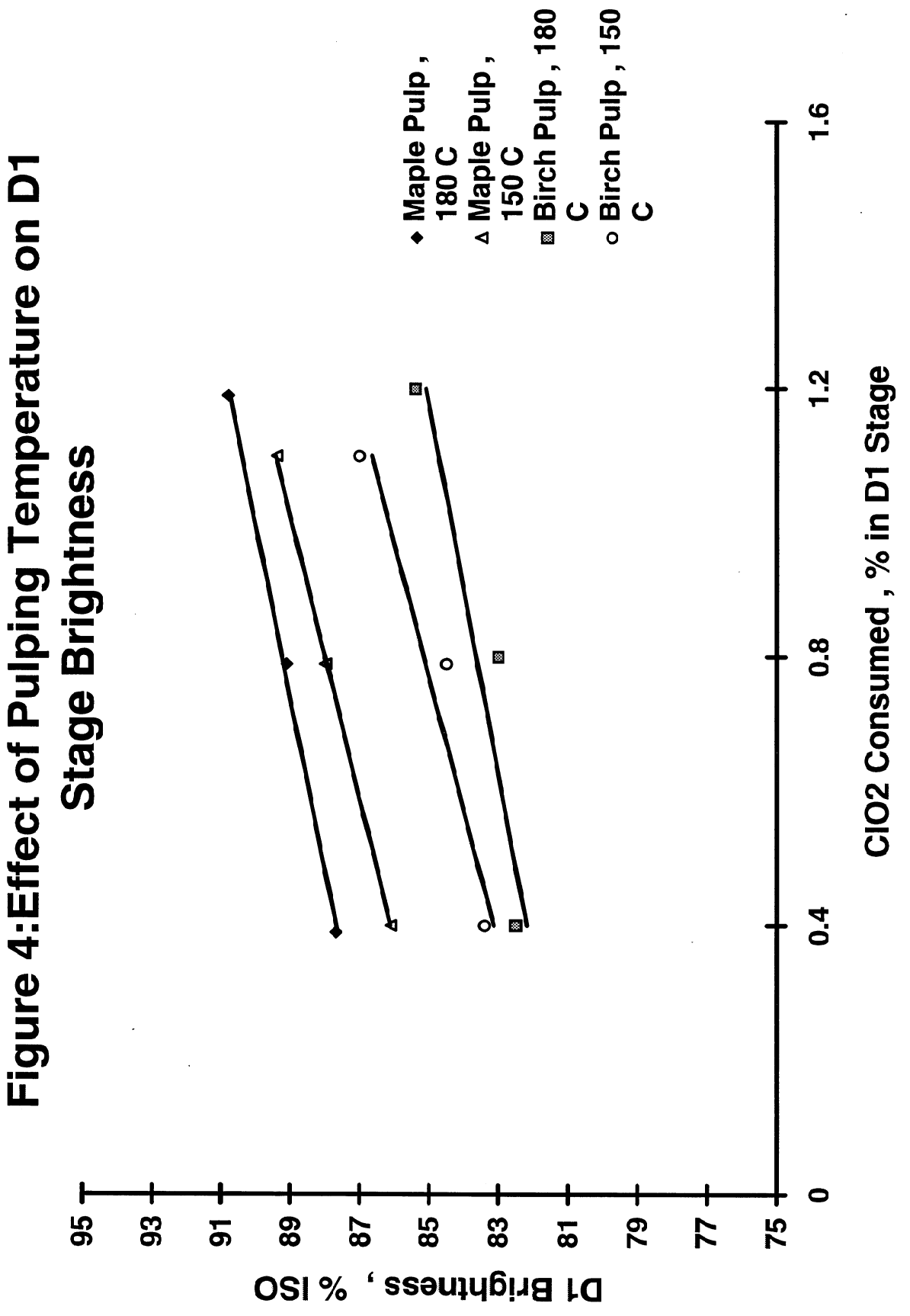


Figure 4:Effect of Pulping Temperature on D1 Stage Brightness
D1 Brightness , % ISO
95
93
91
89
87
85
83
81
79
77
75
0
0.4
0.8
1.2
1.6
ClO2 Consumed , % in D1 Stage
Maple Pulp , 180 C
Maple Pulp , 150 C
Birch Pulp , 180 C
Birch Pulp , 150 C

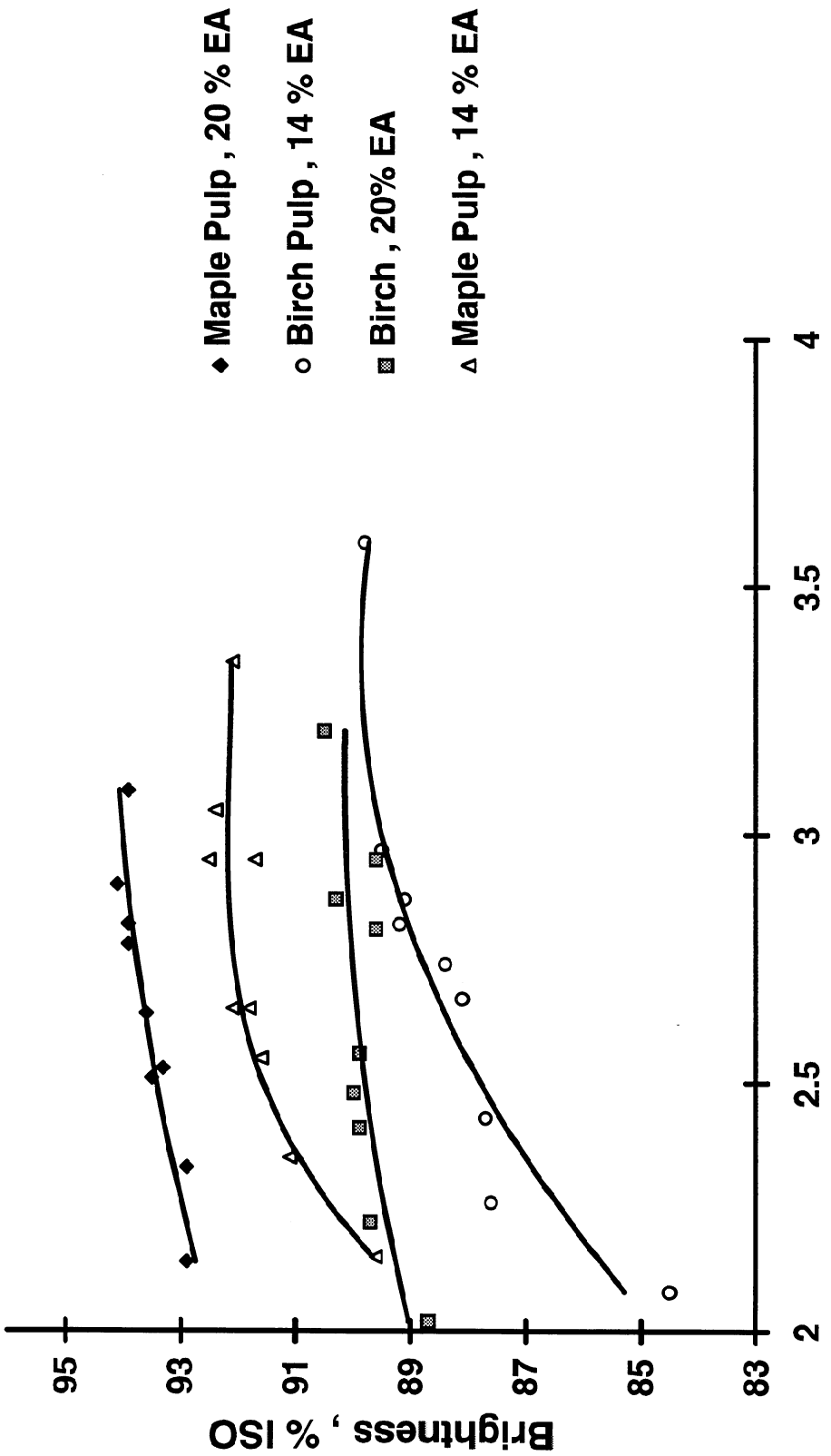
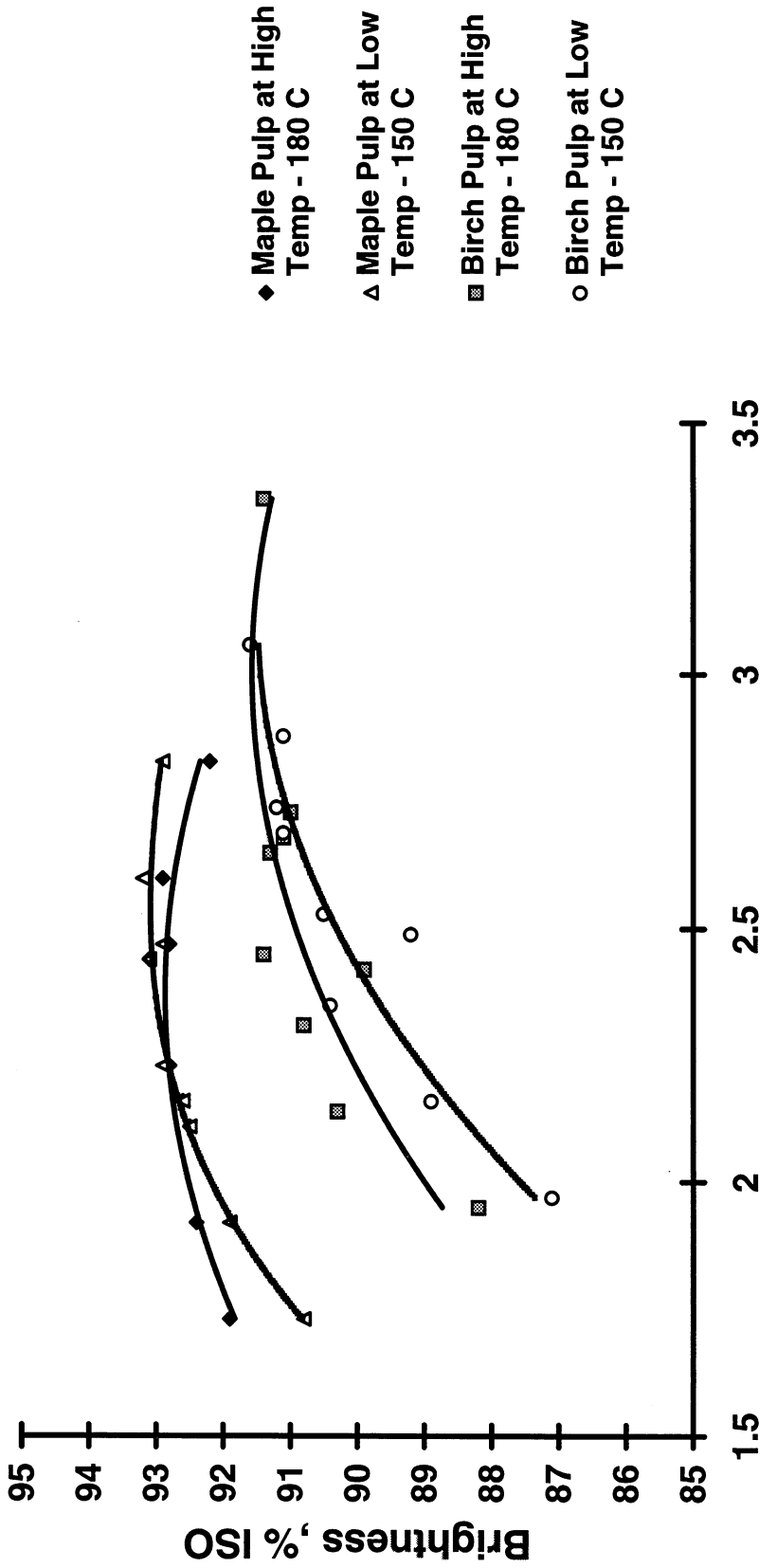


Figure 5:Effect of Effective Alkali on ECF Bleaching [Do(EO)DED] of Hardwood Kraft Pulps
Maple Pulp , 20 % EA
Birch Pulp , 14 % EA
Birch , 20% EA
Maple Pulp , 14 % EA
Brightness , % ISO
95
93
91
89
87
85
83
2
2.5
3
3.5
4
ClO2 Consumed , %

**Figure 6:Effect of Pulping Temperature on ECF Bleaching [ Do(EO)DED ] of Hardwood Kraft Pulps**



# CHEMICAL FUNDAMENTALS OF BLEACHING

Status Report for Project F015

Arthur J. Ragauskas
Lucian Lucia
Donald R. Dimmel
Lenong Allison
Elizabeth Althen

March 24-25, 1998

# DUES-FUNDED PROJECT SUMMARY
# FY 1997-98

| | |
|---|---|
| **Project Title**: | Chemical Fundamentals of Bleaching |
| **Project Number**: | F015 |
| **PAC**: | Chemical Pulping and Bleaching |
| **Division**: | Chemical and Biological Sciences |
| **Project Staff** | |
| **Faculty/Senior Staff**: | Art Ragauskas, Lucian Lucia, Donald Dimmel |
| **Staff**: | Lenong Allison, Elizabeth Althen, to be hired postdoc/tech |
| **FY 97-98 Budget**: | $269,000 |
| **Time Allocation** | |
| **Faculty/Senior Staff**: | 80% |
| **Support**: | 225% |
| **Supporting Research** | |
| **External**: | Improved Selectivity in Ozone Bleaching (4168, USDA) Dimmel<br>High Efficiency $ClO_2$ Delignification (DOE co-funded) Ragauskas<br>Improved Peroxide Bleaching (Georgia Consortium $TIP^3$) Ragauskas |
| **Students**: | Ragauskas Supervisor: James Sealey, Ph.D.; Troy Runge, Ph.D.; Kaaren Haynes, Ph.D.; Michael Zawadzki, Ph.D.; John Werner, M.S. |

## RESEARCH LINE/ROADMAP:

Environmental Performance:

- Reduce emissions of entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule while maintaining global competitiveness.
- Reduce water usage in bleached kraft pulp production to 2500 gallons per ton.

Improved Forest Productivity:

- Increase the yield of kraft-pulp equivalent fiber by 10%

## BROAD PROJECT OBJECTIVES:

Provide a fundamental understanding of the physical and chemical reactions that control lignin and carbohydrate degradation during new bleaching sequences. Understand the reasons for selectivity of reactions that occur in selected pulping and bleaching sequences. The research compliments Project F013 research on bleach process technology. Focus areas are ozone and high efficiency peroxide bleaching, hexenuronic acids, biobleaching, and oxygen delignification.

## SUB-PROJECT OBJECTIVES:

*1. High Efficiency Peroxide Bleaching*

The long term goal of this sub-project is to develop improved methods of using hydrogen peroxide for conventional and pressurized bleaching conditions. Our research thrust is to define how hydrogen peroxide reacts with lignin, to allow the rational design of new peroxide bleaching technologies.

*2. Influence of Hexenuronic Acids on Bleaching*

The research goal of this sub-project is to determine to what extent hexenuronic acids influence modern North American pulping and bleaching operations. For those operations that are effected by hexenuronic acids, new technologies will be developed to minimize their effects.

*3. Biobleaching Studies*

The long term goal of this sub-project is to develop new enzymatic-based bleaching technologies for kraft pulps that will improve yield and physical properties of the final product.

*4. Ozone Bleaching*

Cellulose can potentially be depolymerized as a result of attack by ozone directly, by radicals derived from ozone decomposition in water, by radicals from ozone-phenol reactions, and/or by radicals from secondary decomposition of ozone-organic intermediates. The goal of this research project is to clarify the relative importance of these reaction pathways.

*5. Oxygen Delignification*

Fundamental studies of oxygen delignification for to obtain high yield, high strength pulps will address (1) the lack of selectivity for delignification versus cellulose damage after 40-50% delignification of kraft pulp and (2) the delivery of oxygen to lignin.

## SUMMARY:

*1. High Efficiency Peroxide Bleaching*

Lignin studies of D(EOP) and DE bleached kraft pulps were completed. Data analysis suggested that condensed phenolic groups are resistant to a $D_0$ stage. Residual lignin studies and peroxide bleaching studies of methylated pulp suggests that alkaline peroxide is more effective at chromophore removal than delignification.

*2. Influence of Hexenuronic Acids on Bleaching*

The temperature and acid conditions needed to remove hexenuronic acids was studied. Hexenuronic acids were shown to be one of the main components involved in binding non-process elements (NPE) to kraft pulp. Removal of hexenuronic acids was shown to substantially improve pulp bleachability of hardwood kraft pulps. Polysulfide kraft cooking was shown to have little influence on the formation of hexenuronic acids. In contrast, AQ appeared to favor the formation

of hexenuronic acids. Preliminary investigations suggest that the effective alkali influences hexenuronic acid formation during cooking.

*3. Biobleaching Studies*

New mediators were studied for the laccase/mediator delignification system. For a softwood oxygen delignified kraft pulp these new mediator allowed for >50% delignification with less than 3% of the of the typical enzyme charge. Preliminary studies demonstrated that laccase/mediator systems were effective at delignifying high kappa kraft pulps.

*4. Ozone Bleaching*

The ozone research in Project F015 is being conducted as part of Project 4168 (please refer to its Project Summary for a summary).

*5. Oxygen Delignification*

These studies are just beginning. During the last four months, literature research and proposal writing have comprised the bulk of the activities.

## GOALS FOR FY 97-98:

The ozone goals are listed under Project 4168; the goals for the remaining three months of FY 97-98 for the other areas are:

- Study bleaching chemistry of new laccase mediators.
- Investigate $D_0$ (EOP) bleaching chemistry.
- Perform a preliminary investigation of several untried methods of effecting singlet oxygen delignification of kraft pulps. For example, one method envisioned is development of a pressurized chamber with a light source allowing for the reinforced treatment of pulps with singlet oxygen and oxygen (akin to oxygen and hydrogen peroxide bleaching). Pending completion of the reactor, typical experiments will include performing oxygen-reinforced singlet oxygen bleaching (bubbling oxygen) of kraft pulp in a Photochemical Reaction Chamber with a Hanovia Lamp at ~10 different irradiation times, 10 different consistencies, and 2 different wavelengths. The reactions will be performed in the absence of singlet oxygen sensitizers as well as in the presence of various oxygen singlet sensitizers (high-energy absorbers such as acetone and low-energy such as methylene blue). Any changes in kappa numbers by singlet oxygen will be verified by using various controls such as superoxide dismutase or β-carotene.
- Several experiments with charged oxygen sensitizers, such as methylene blue will be performed in conjunction with iodine. Iodine is known to complex with aromatics to form polarized charge-transfer complexes which may aid in coulombically attracting methylene blue in the vicinity of the lignin to produce singlet oxygen which can be quenched (i.e., reaction) by lignin to yield oxidation products. Experimental protocols will include varying the concentration of iodine to lignin (5-10 concentrations), the concentration of sensitizer (5-10 experiments), and the time of irradiation (5-10 experiments), and monitoring kappa number changes.

## High Efficiency Peroxide Bleaching *by Art J. Ragauskas*

### Summary of Past Results

Peroxide studies have focused on determining the relationship between peroxide delignification chemistry and the type of lignin present in the pulp. To accomplish this goal, we have examined the structure of residual lignin before and after peroxide bleaching of conventional and oxygen delignified softwood kraft pulps.

The results from peroxide bleaching of conventional and $O_2$ delignified kraft pulps suggest that a portion of the lignin can be readily oxidized with alkaline peroxide. Lignin analysis indicates that non-condensed phenoxy groups are readily oxidized by peroxide. Residual lignin from a peroxide bleached pulp is usually enriched in condensed lignin structures.

The delignification properties of an acidic pressurized peroxide stage were examined with a conventional southern softwood kraft pulp. Preliminary studies suggested that 50% delignification could be achieved by this procedure but this was accompanied by a severe loss in pulp viscosity.

Research studies have also examined the intrinsic reactivity of lignin functional groups toward alkaline peroxide. As an initial study, a softwood kraft pulp was chemically enriched with ortho-quinones and then bleached with peroxide. Pulp bleaching studies suggested that a small improvement in delignification could be achieved if pulps were enriched with this functional group. Counter-cation effects on an alkaline peroxide bleaching stage were also examined. It was demonstrated that the extent of delignification varied according to the size of the cation. For routine P and pressurized peroxide (P*) bleaching of kraft pulps, the order of bleaching efficiency based on cation was $(CH_3)_4NOH > CsOH > KOH > LiOH > NaOH$.

## Research Goals

FY 1997-98 goals for this section of project F015 are listed below:

1. Examine inverted "PHT" bleaching protocol.

2. Determine the structure of residual lignin and bleach effluents after bleaching SW and HW kraft pulps with D(EOP).

3. P and P* bleaching of modified kraft pulps.

These research goals have been accomplished over this past fiscal year and the results of these investigations are summarized in this report.

## Results

**Goal 1 :** Prior peroxide bleaching studies had suggested that most kraft pulps have two "types" of lignin with respect to alkaline peroxide delignification. Structure analysis studies had suggested that for peroxide bleaching a portion of the lignin can be readily oxidized. Once this lignin is oxidized the remaining material is very resistant to reactions with alkaline peroxide and requires either high temperature/high pressure or chemical activation. Based on these observations it was hypothesized that inverting the temperature profile of a $P_{HT}$ stage could facilitate removal of peroxide resistant lignin. A routine $P_{HT}$ stage has a temperature profile of 105-110°C for ca. 20 minutes and this is then lowered to 90°C for one hour. Inversion of this temperature profile could potentially enhance the oxidation of peroxide resistant lignin.

This hypothesis was tested by bleaching three softwood kraft pulps with DP'. The $D_0$ stage employed a 0.20 kappa factor. After bleaching for 30 min at 50°C the pulp was filtered, washed, and placed in a pressurized Parr reactor and treated with alkaline peroxide. The P-stage was performed with 1.0% peroxide and 2.0% NaOH. Table 1 summarizes the experimental conditions employed for the peroxide stages.

Table 1. Results of bleaching softwood kraft pulps with a 0.20 k.f. $D_0$ stage followed by a "P"-stage.

| *Kappa # of* | *Kappa # after P-Stage* | | |
|---|---|---|---|
| *Brownstock* | *EOP*[1] | *$P_{HT}$*[2] | *Inverted $P_{HT}$*[3] |
| 26.4 | 2.6 | 2.6 | 2.6 |
| 22.4 | 2.4 | 1.7 | 2.5 |
| 15.4 | 2.4 | 2.2 | 2.0 |

[1]EOP: 90°C, 120 min., 10% csc, $O_2$: 60 psi; $P_{HT}$: [2]initially 110°C for 15 min then 90°C for 105 min., 10% csc, $O_2$: 60 psi. Inverted $P_{HT}$: [3]initially 90°C for 105 min then 110°C for 15 min., 10% csc, $O_2$: 60 psi

This data indicates that the inverted $P_{HT}$ fails to enhance the delignification properties of alkaline peroxide under the conditions studied. Also of interest is the observation that not all three pulps responded favorably to the $P_{HT}$ stage. The factors contributing to this effect are currently unknown. However, it is suspected that the metal profile of the pulps may play a contributing factor to this effect.

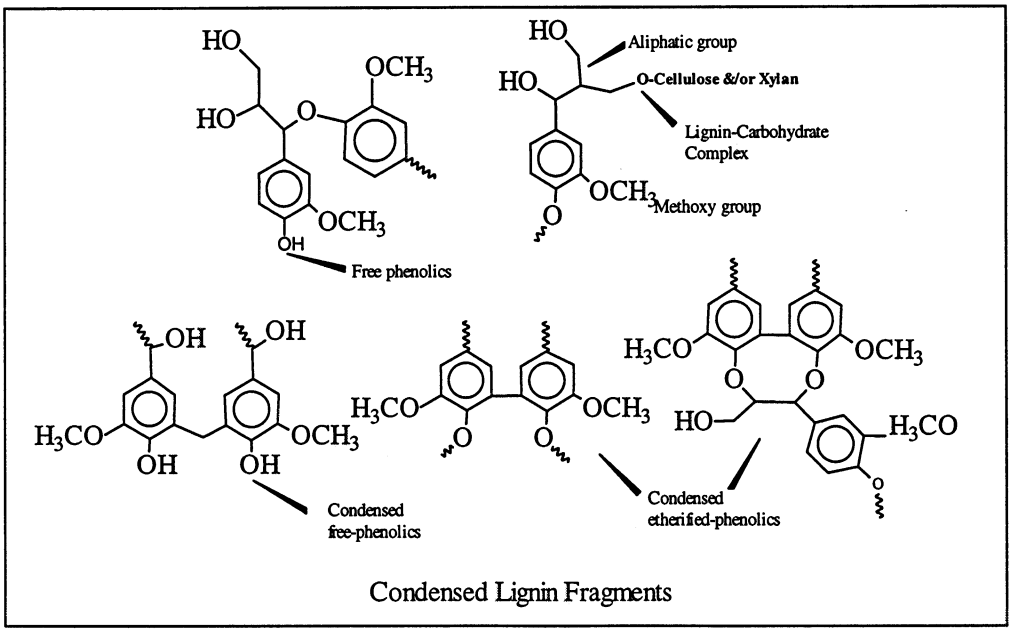
**Goal 2:** One of our central research themes in project F015 is the analysis of residual lignin. In the long term, it is anticipated that these results will provide a fundamental understanding of how lignin is altered during kraft pulping and bleaching. This knowledge will facilitate the rational development of new and improved bleaching technologies. For fiscal year 1997-98, our goal was to study the changes in residual lignin for SW and HW kraft pulps after D(EOP).

This goal was accomplished following our usual procedure that entails:

1. Pulp bleaching;
2. Lignin isolation via an acidic dioxane extraction procedure;
3. Lignin analysis by NMR.

The objective of these studies was to determine how a D(EOP) treatment alters the nature of residual lignin in kraft pulps. As reviewed in the 1997 spring PAC presentation, NMR analysis of lignin can readily quantify various functional groups present in residual lignin, including methoxy, non-condensed phenoxy, condensed phenoxy, carboxylic acids, and aliphatic groups (see Fig. 1).

Figure 1. Residual functional groups in kraft lignin.



The D(EOP) bleaching studies were performed with a commercial softwood and hardwood kraft pulp. Each pulp was bleached with a 0.20 and 0.15 k.f. of chlorine dioxide and then extracted with an E and (EOP)-stage. Table 2 summarizes the experimental conditions employed.

Table 2. D(EOP) conditions used to bleach a softwood and hardwood kraft pulp.

| *Bleaching Stage* | *Experimental Conditions* |
|---|---|
| $D_0$ | 0.20, 0.15 k.f. $ClO_2$, 3% csc, 45°C, 45 min. |
| E | 2% NaOH, 10% csc, 70°C, 75 min. |
| EOP | 0.5% $H_2O_2$, $O_2$: 60 psi, 2% NaOH, 10% csc, 70°C, 75 min. |

The DE and D(EOP) kraft pulps were extracted with acidic dioxane. The lignins isolated from the acidic dioxane stages were analyzed by $^1H$ NMR. The results of these studies are summarized in Figures 2 - 5.

Figure 2. Content of carboxylic acids, non-condensed phenolics, and condensed phenolics present in a SW kraft pulp before and after D(EOP) or DE (k.f. 0.20).

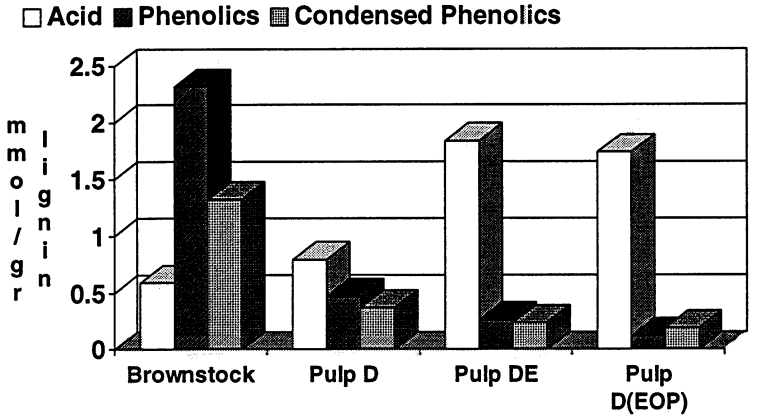
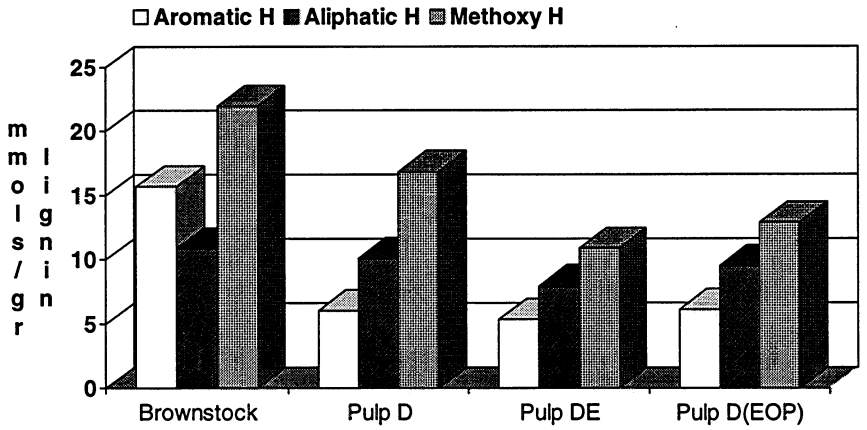
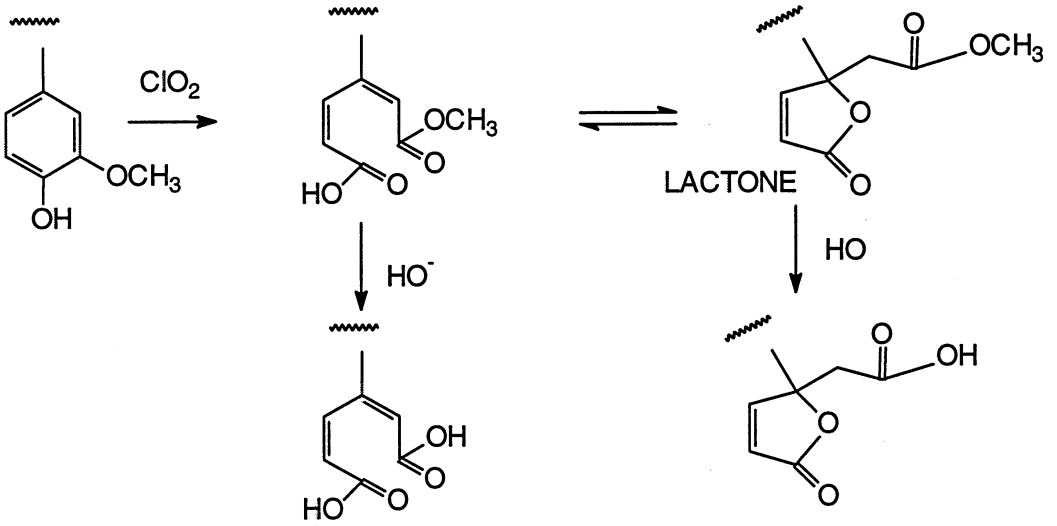



Figure 3. Content of methoxy, aliphatic, and aromatic protons in a SW kraft pulp before and after D(EOP) or DE (k.f. 0.20).



Analysis of the residual lignin from the softwood kraft pulps before and after bleaching suggests that the residual lignin is enriched in acid groups as bleaching progresses. Interestingly, the acid content increase is greater between the D and E stages than the brownstock and D stage. This is presumably due, in part, to the conversion of muconic esters to the corresponding acids during the alkaline extraction stage (see below).




An examination of the condensed and non-condensed phenolics in the brownstock and post $D_0$ stage, (see Fig. 2) indicates that chlorine dioxide substantially reduces free phenols. A comparison of the relative amounts of condensed and non-condensed phenols removed during the $D_0$ stage suggests that the non-condensed phenol structures react more readily with chlorine dioxide. This trend in reactivity for condensed and non-condensed phenols appears to continue in the alkaline extraction stage. The loss of methoxy groups (see Fig. 3) in the residual lignin suggests that chlorine species such as, hypochlorous acid or chlorine are de-methoxylating lignin during a $D_0$ stage.

NMR characterization of acid-precipitated lignin from the alkaline extraction stage compliments the results observed in the residual lignin studies (see Fig. 4). The phenoxy content is very low with the ratio of condensed to non-condensed phenoxy groups being approximately 1:1. The effluent lignin is also enriched in acids groups, but our analysis may underestimate the amounts of acid groups present in the effluent since our isolation method yields only that material that can be acid precipitated (Note: modifications to this procedure will be examined the next fiscal year). The differences in the amounts of acid groups detected in the alkaline effluents from the pulp bleached with a k.f. of 0.20 vs. 0.15 is difficult to explain and will need further investigation.

The structure of residual lignin from HW kraft pulps was also examined this fiscal year. A comparison of the amounts of phenolic groups in the residual lignin of a hardwood kraft after D(EOP) using a k.f. of 0.20 vs 0.15 suggests that the higher charge of $ClO_2$ removes significantly more free phenolics (see Fig. 5). The increased oxidation of the lignin is also accompanied by an increased formation of acid groups.

Figure 4. Content of carboxylic acids, non-condensed phenolics, and condensed phenolics present in the effluent from a SW kraft pulp bleached D(EOP) or DE (k.f. 0.20 & 0.15).

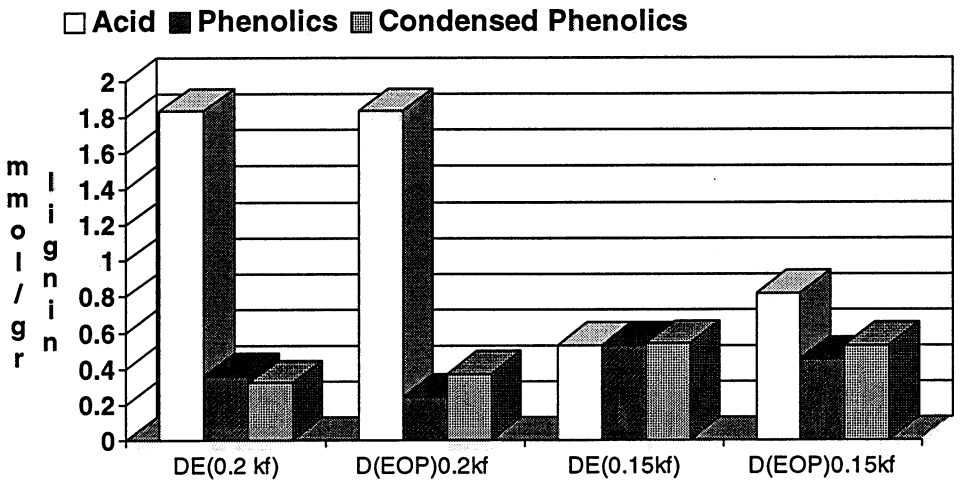
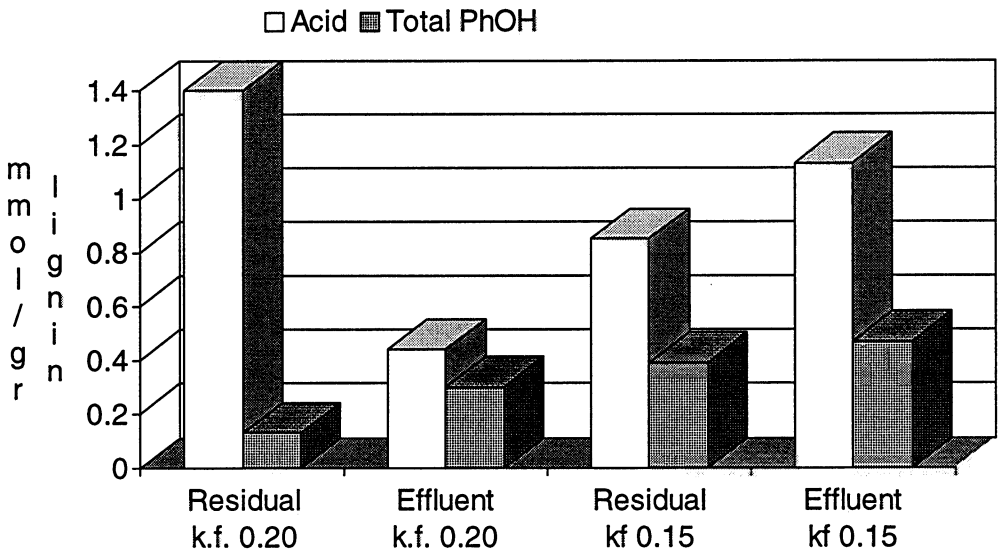



Figure 5. Content of carboxylic acids and total phenolics present in bleached D(EOP) pulp and the alkaline extract effluents.




The use of peroxide in an EOP stage does not dramatically alter the structure of residual lignin. The results presented in this report show very little difference in lignin structure between the E and (EOP) residual lignins. Recent Ph.D. studies by Runge and Zawadzki tend to support this conclusion. Molecular weight studies by Runge (see Advances in Understanding the Basics of the First Alkaline Extraction Stage in Bleaching Runge, T.; Ragauskas, A.; Froass, P.1997 Pulping Conference: Proceedings (TAPPI): 603-608 (October , 1997)) suggest that the addition of peroxide to an E-stage is, in part, spent on reactions with dissolved lignin. Studies by Zawadzki indicate that peroxide in a EOP stage is effective at removing quinones from the pulp. In summary, alkaline

peroxide added to an EOP stage appears to be more effective at removing chromophores from the pulp than oxidizing the residual lignin.

Future studies will be directed towards identifying the optimal charges of peroxide and chlorine dioxide to be used to achieve high brightness bleached kraft pulps.

Addendum. The bleaching of chemistry D(EO) with SW kraft pulps has been investigated. The results of these studies will be presented at the upcoming Int. Pulp Bleaching Conference and a copy of the manuscripts is included in this report.

NOTE: The report for Goal 3 of this sub-project follows the Ragauskas/McDonough paper.

# FUNDAMENTAL ASPECTS OF RAPID $ClO_2$ DELIGNIFICATION OF CONVENTIONAL AND EXTENDED MODIFIED KRAFT PULPS

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## ABSTRACT

The bleachability of conventional and extended modified kraft pulps was studied with the bleaching sequence D(EO). These studies demonstrated that high kappa conventional pulps exhibited slightly improved bleaching properties over low kappa pulps. In contrast, the extended modified pulps were found to exhibit equally good bleachability throughout the kappa number range (29-16) studied. Analysis of the residual lignin structure of the bleached pulps suggested that the residual lignin after a $D_0$ or D(EO) stage was extensively oxidized. Structural analysis studies suggested that the amount of condensed phenolic units present in the residual lignin influenced the bleachability properties.

## INTRODUCTION

Recently proposed environmental regulations in North America and continued consumer demand for high-brightness, high-strength pulps has ensured the continued use of chlorine dioxide for bleaching kraft pulps. The need to minimize bleaching costs, improve pulp yields, and enhance the performance of fully bleached pulps have become important research issues. One of the research challenges ahead is to find new ways to improve the delignification and brightening properties of chlorine dioxide.

From a mill perspective, it is well known that the bleachability of kraft pulps can vary substantially. Pulp bleachability can be influenced by a wide array of factors including process variables, such as the efficiency of pulp washing (1) to fundamental chemistry issues, including the structure of residual lignin (2) and carbohydrates in the fiber.(3)

Teder and Sjostrom (4) have demonstrated that alkaline sulfite pulping yields pulps with significantly improved bleachability properties with respect to kraft pulps. Classical studies by Germgard (5) have shown that post-oxygen delignified kraft pulps are less bleachable than pre-$O_2$ kraft pulps with chlorine dioxide. Recently, studies by Buchert et al. (6, 7) have significantly advanced our knowledge on how carbohydrates, specifically hexenuronic acids, can impact pulp bleachability.

It is also well known that the structure of residual lignin can influence pulp bleachability, especially with chlorine dioxide. This dependency is due, in part, to the reactivity of chlorine dioxide with phenoxy groups. Kumar et al. (8) studied differences in pulp bleachability between

RDH and conventional kraft pulps and suggested a correlation between phenoxy content of the residual lignin and bleachability. Gellerstedt and Al-Dajani (9) have reported that the bleachability of softwood kraft pulps with chlorine dioxide or hydrogen peroxide was influenced by kraft cooking conditions. These differences in bleachability were attributed to differences in residual lignin content, lignin-carbohydrate complexes, and condensed carbohydrates. Froass et al. (10) observed that for softwood kraft pulps, bleachability was influenced by the kappa number of the pulp and the pulping process employed. The total available chlorine (TAC) consumed per unit kappa number reduction in the D(EO) sequence was found to decrease as the kappa number decreased despite the fact that the lower kappa pulps were found to have higher amounts of phenoxy groups. A closer examination of the residual lignin structure prior to bleaching suggested that the amounts of condensed phenolics increased as delignification was extended and it was hypothesized that these units were detrimentally influencing pulp bleachability.

In this paper, we examine the relationship between pulp bleachability and chlorine dioxide delignification for a series of conventional (CK) and pulps from extended modified kraft cooks (EK pulps). The bleachability properties of these pulps were examined after $D_0$ and D(EO). The $D_0$ stage was performed using a kappa factor of 0.05 and 0.20 at 10% consistency with high shear mixing and a $ClO_2$ retention time of 1 min. Previous studies by Schwantes and McDonough (11) have shown that substantial delignification of kraft pulps can be accomplished with reaction times significantly less than what is employed in a typical $D_0$ stage. The resulting pulps were then alkaline extracted in an oxygen reinforced stage. Pulp bleachability, measured as TAC/Δ(kappa number), was determined after the $D_0$ and (EO) stage. Residual lignin was isolated before and after each stage and changes in lignin functional groups were determined employing modern NMR methods. This paper summarizes the results of these studies.

## EXPERIMENTAL

### Materials

All chemicals were commercially purchased and used as received except for p-dioxane, which was purified by distillation over sodium borohydride. All pulps were prepared from a single *Pinus taeda* tree grown in the southeastern part of the USA. The tree was debarked, chipped, and screened. On average, chip thickness varied between 2 - 8 mm.

### Kraft Pulping

The kraft pulping experiments were performed at Alhstrom's pilot facilities in Glenns Falls, NY. Established procedures were used to simulate conventional and extended modified continuous (i.e., Lo-Solids®) cooking. (12) Table 1 highlights some of the pulping parameters employed and physical pulp properties.

**Table 1.** Pulping conditions and pulp properties from CK and EK pulps.

| | Conventional Kraft Pulps (CK) | | | Extended Modified (EK) Continuous Kraft Pulps | | |
|---|---|---|---|---|---|---|
| Kappa # | 33.0 | 21.3 | 14.7 | 29.3 | 19.1 | 16.0 |
| Viscosity mPa | 32.6 | 22.6 | 13.3 | 43.4 | 25.5 | 19.2 |
| Max. Temp °C | 168 | 170 | 171 | 160 | 166 | 170 |
| H-Factor | 1201 | 1999 | 3496 | 2003 | 3362 | 4489 |
| Total EA Consumed %on wood | 14.8 | 15.4 | 16.7 | 14.1 | 15.0 | 16.6 |

## Rapid Do

Employing the quantum reactor, a 3% consistency pulp mixture was heated to 45°C and the pH was adjusted to either 5.0 or 4.0 for kappa factor 0.20 and 0.05 $ClO_2$ bleaching experiments, respectively. $ClO_2$ (kappa factor of either 0.05 or 0.20) was added into the quantum reactor and the pulp was mixed for 30 sec at 15 Hz and the mixer was then stopped for 30 sec, after which a quenching solution of aqueous $Na_2SO_3$ (mass $Na_2SO_3$ added=mass applied $ClO_2$ x 4.67 ) was injected. The pulp mixture was then stirred for an additional 30 sec., filtered, and characterized. Kappa number was then determined.

## (EO)-Stage

The pulp from the Do stage was thickened to 25% consistency, without washing, thoroughly disintegrated and added to a pin mixer. The consistency was adjusted to 10% and the pulp was then extracted under typical (EO) conditions: NaOH charge was chosen to yield a terminal pH of 10.7-11.5. The (EO) stage was performed at 70°C for 60 min. The initial $O_2$ pressure was 60 psig and this was decreased 10 psig every 5 min. At the end of the (EO) stage, the pulp consistency was adjusted to 3%, the effluents were collected, and the pulp was thoroughly washed.

## Residual Lignin Isolation

Isolation of residual lignin from the softwood kraft pulps was accomplished employing standard literature methods (13, 14, 15). In brief, air-dried pulp (40 gr oven-dry weight) was added to an aqueous 1.00 N HCl (100 ml), p-dioxane (900 ml) solution and this mixture was then refluxed for 2 hr under an argon atmosphere. The mixture was then filtered, concentrated, and purified by precipitation. This procedure afforded, on average, 30-55% yield of residual lignin as summarized in Table 2.

## $^1$H NMR Analysis of Residual Lignin

The lignin samples were dissolved in anhydrous DMSO-$d_6$. Sodium-3-trimethylsilyl propinate-2,2,3,3-$D_4$ was added as an internal standard and the samples were analyzed using a 400 MHz Bruker DMX NMR spectrometer. The analyses were accomplished employing a $\pi/2$ pulse, 25-sec delay, 12,000 Hz sweep width, and 240 transients. The FID was fourier transformed with 1 Hz of line broadening and one degree of zero filling. Data analysis was accomplished using the method recently reported by Li and Lundquist.(16)

**Table 2.** Yield of lignin recovered from brownstock and bleached pulps.

| CK Pulp | %Lignin Yield[a] | EK Pulp | %Lignin Yield |
|---|---|---|---|
| CK32.4:pulp | 58 | EK29.3:pulp | 52 |
| $D_0$ | 35 | $D_0$ | 30 |
| (EO) | 36 | (EO) | 36 |
| CK21.3:pulp | 54 | EK19.1:pulp | 48 |
| $D_0$ | 29 | $D_0$ | 30 |
| (EO) | 29 | (EO) | 28 |
| CK14.7:pulp | 57 | EK15.6:pulp | 55 |
| $D_0$ | 30 | $D_0$ | 28 |
| (EO) | 39 | (EO) | 29 |

[a]% lignin recovered=(mass of lignin recovered)/(kappa number of pulp x oven dry weight of pulp x 0.15%)

## $^{31}$P NMR Spectroscopy

Lignin samples were phosphorylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane following the procedure of Argyropopoulos (17) and analyzed by $^{31}$P-NMR.

## RESULTS AND DISCUSSION

### Bleachability of Kraft Pulps

Recent studies at IPST have shown that the rapid kinetics of chlorine dioxide delignification of kraft pulps can be utilized for bleaching provided that good uniform mixing can be accomplished. Preliminary studies reported by Schwantes, demonstrated that most of the delignification of a $D_0$-stage is accomplished within the first 1-2 minutes of bleaching, provided that the bleaching chemical is uniformly distributed throughout the bleaching reactor.(7) This type of very short bleaching stage, referred to as Rapid $D_0$, reduces AOX formation and offers significant savings in bleach plant capital equipment. This paper examines the results of applying this process in the delignification of a series of softwood kraft pulps manufactured under conventional and conditions and conditions that correspond to Lo-Solids® cooking, a modified kraft pulping process designed to allow delignification to be extended to low kappa numbers without loss of pulp quality. This was of interest because the short retention time is expected to yield bleached pulps having lignins whose structural features are unaffected by secondary reactions. In what follows, the Lo-Solids® pulps are referred to as extended (EK) pulps. The results of the bleaching studies are summarized in Table 3.

The results summarized in Table 3 indicate that the conventional pulps exhibited only slightly improved bleachability at higher lignin contents when the $ClO_2$ retention time is kept short. The EK pulps were equally bleachable at high and low lignin contents under these conditions. These results differ somewhat from those of earlier studies by our group (18) indicating that the decreased bleachability of low-kappa pulps at normal $D_0$ retention times is related to inhibition of reactions that occur after the initial phase.

**Table 3.** Bleachability of CK and EK pulps towards Rapid $D_0$ and EO.

| Pulp | k.f. | TAC | Δ Kappa | TAC/Δ Kappa |
|---|---|---|---|---|
| CK-32.4 | 0.05 | 1.62 | D - 5.9<br>EO-13.6 | 0.274<br>0.119 |
| CK-32.4 | 0.20 | 6.48 | D - 15.3<br>EO-24.3 | 0.423<br>0.267 |
| CK-21.3 | 0.20 | 4.26 | D - 9.2<br>EO-15.3 | 0.463<br>0.278 |
| CK-14.7 | 0.20 | 2.94 | D - 6.5<br>EO-10.6 | 0.452<br>0.277 |
| LS-29.3 | 0.05 | 1.46 | D - 5.1<br>EO-13.0 | 0.286<br>0.112 |
| LS-29.3 | 0.20 | 5.86 | D - 13.7<br>EO-22.2 | 0.428<br>0.264 |
| LS-19.1 | 0.20 | 3.82 | D - 8.8<br>EO-14.6 | 0.434<br>0.262 |
| LS-15.6 | 0.20 | 3.12 | D - 6.9<br>EO-11.8 | 0.452<br>0.264 |

The EK pulps were modestly easier to delignify than the conventional pulps, requiring a $ClO_2$ charge that was an average of 4% lower than in the case of CK for a given kappa number reduction measured after the (EO) stage. The TAC/Δκ values were larger than normally observed at normal retention times in the $D_0$ stage because no credit was taken for the unutilized residual remaining after only one minute. In order to limit the $D_0$ reaction time to exactly one minute, it was necessary to stop the reaction by injection of sulfite, which destroyed the residual and precluded its measurement. It is for this reason that, in practical applications, low kappa factors are recommended for Rapid $D_0$.

**Residual Lignin Analysis**

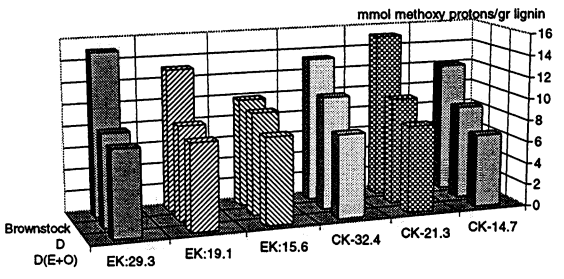
The difference in bleachability between the CK and EK pulps suggests that it may be possible to tailor pulp properties to a bleaching chemical. However, before such a strategy can be rationally designed, the fundamental principles involved in bleachability must be determined. Over the last 10 years, our knowledge of residual lignin structure in kraft pulps has grown tremendously. Early studies by Gierer (19), Gellerstedt (20,21,22) and Dimmel (23) documented the changes in lignin structure during a kraft cook. These studies established that as cooking proceeds, numerous changes occur in residual lignin, including an increase in residual lignin phenoxy content and a decrease in β-O-aryl ether content.

Having established these important pulping reactions, several researchers have now focused on elucidating how process changes in the kraft pulping can moderate the structure of residual lignin. Studies by Hortling et al.(24) have compared the differences in residual lignin that occur between Superbatch and conventional kraft pulps. Gellerstedt (9) has reported differences in bleachability of Scandinavian softwood kraft pulps dependent upon how they are cooked. Jiang and Argyropoulos (25) have found that residual lignin from modified continuous kraft pulping procedures has lower amounts of condensed phenolic units and higher amounts of carboxylic acids as compared to lignin isolated from conventional kraft pulps. Froass et al. have shown that pulps prepared under simulated conventional and EMCC® conditions exhibited differences in residual lignin structure and bleachability (10). It was hypothesized in these latter studies that condensed phenoxy groups and β-O-aryl ether groups may influence chlorine dioxide bleachability of kraft pulps.

This study seeks to further examine the relationship between pulp bleachability and residual lignin structure. The pulps examined in this study were all prepared from a common wood source. This facilitated comparisons of residual lignin structures before and after bleaching with D(EO).

In an earlier report, we examined the structure of the residual lignin present in the kraft pulps employed in this bleaching study. The results of these studies suggested the CK and EK pulps had comparable lignin functional groups at kappa numbers of approximately 30. As delignification was extended, the CK pulps were found to have higher amounts of phenolics and methoxy groups than the EK pulps. To further explore the relationship between bleachability and residual lignin structure, we isolated residual lignin structure after the Rapid $D_0$ and (EO) stages employed in the current study. The residual lignin samples isolated from these pulps were analyzed by $^1H$ NMR according to the method of Li and Lundquist.(16) This procedure provides a convenient method of determining the concentration of phenolic units, carboxylic acids, and methoxy groups in residual lignin. The changes in methoxyl content for the unbleached and bleached pulps is summarized in Figure 1.

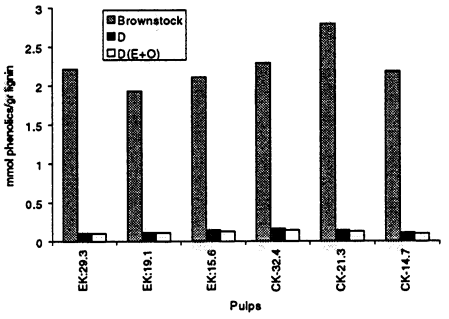
Figure 1. Methoxyl proton content for residual lignin from brownstock, D, and D(EO) CK and EK pulps as determined by $^1$HNMR.




The decrease in methoxy content from the brownstock to the Rapid $D_0$ bleached pulps is a result of the demethoxylation chemistry associated with chlorine species in the $D_0$ stage. The additional decrease in methoxy content measured after the (EO) stage can be attributed, in part, to the hydrolysis of muconic acid methyl esters during alkaline extraction. Nonetheless, the largest loss in methoxy content occurred during the Rapid $D_0$ stage.

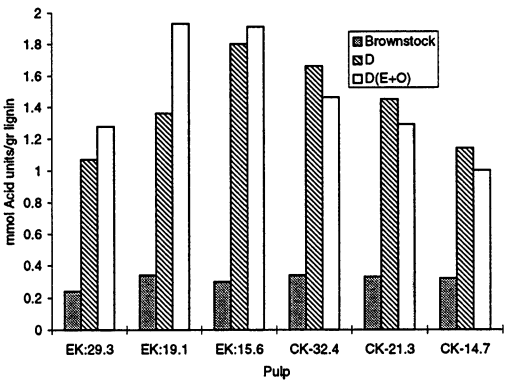
Another group of significant interest in chlorine dioxide bleaching is the phenolic unit. The use of proton NMR provides a method of monitoring the changes in the concentration of this functional group as pulping and bleaching proceeds. The results of this analysis for the LS and CK pulps are summarized in Figure 2.

Figure 2. Phenoxy proton content for residual lignin from brownstock, D, and D(EO) CK and EK pulps as determined by $^1$H NMR.




The results of this analysis suggested that the Rapid $D_0$ stage was efficient at removing most of the phenolics from the residual lignin isolated for these studies.

Figure 3. Carboxylic acid proton content for residual lignin from brownstock, D, and D(EO) CK and EK pulps as determined by $^1$H NMR.

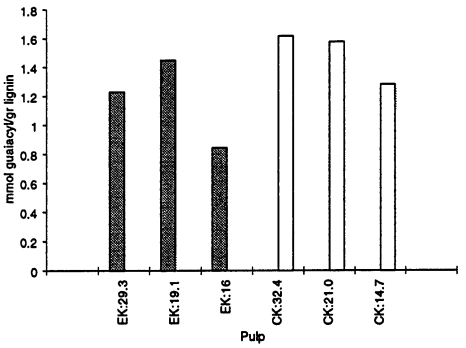



As expected, the extensive oxidation of lignin yielded a residual lignin that contained a significant enrichment of acid groups, as summarized in Figure 3.

In light of these substantial structural changes in the residual lignin, the parameters contributing to differences in bleachability become more difficult to elucidate. Nonetheless, a close inspection of the residual lignin components of the starting pulps did suggest a possible contributing factor. The CK pulps studied in this report have both higher noncondensed and condensed phenoxy structures. Perhaps

most notable is the increased amounts of condensed phenolics, as shown in Figure 4.

Figure 4. Condensed guaiacyl proton content for residual lignin for CK and EK pulps as determined by $^{31}P$ NMR.




The results of the $^{31}P$ NMR analysis of the phosphitylated residual lignin samples suggests that the conventional pulps have higher amounts of condensed lignin than the EK pulps. Hence, the CK pulps, despite having higher total phenolic concentration, are less reactive to chlorine dioxide due possibly to the increased amounts of condensed phenolics. [Note: Lignin phosphitylation/ $^{31}P$ NMR analysis was employed so as to facilitate comparisons with our previous studies].

It is interesting to compare the results of this analysis with our prior studies on conventional and EMCC® pulps. The results of pulp bleachability studies for these latter pulps and the phenolic content of the residual lignins is summarized in Table 4.

Table 4. Kraft residual lignin structure and bleachability of EMCC® and conventional softwood kraft pulps bleached via $D_0$(E+O).

| Pulp[1] | TAC[2]/Δ Kappa | mmol total phenolics/gr lignin[3] | mmol condensed phenolics/gr lignin |
|---|---|---|---|
| E:29 | 0.21 | 2.07 | 0.91 |
| E:18 | 0.22 | 2.15 | 0.94 |
| C:28 | 0.21 | 2.07 | 0.89 |
| C:18 | 0.23 | 2.29 | 0.99 |

[1]E pulps were prepared via simulated EMCC® conditions, C pulps were prepared under simulated conventional kraft conditions, kappa number of the unbleached softwood kraft pulp is given after the letter; [2]pulps were bleached under conventional $D_0$ (0.20 k.f.) (E+O)-stages, see Froass et al. for experimental further details; [3]lignin isolated in the same manner as employed in this paper.

Our results with the CK pulps mirror the results summarized in Table 5. As the kappa number of the CK or C pulp was lowered from the 30's to the mid-20's the phenoxy content increases and bleachability decreases. In each case, this can be attributed to the increase in condensed phenolic lignin units. The EK pulps do not have the same profile of condensed lignin and presumably this explains the differences in bleachability between the EK pulps and the E pulps in Table 4.

## CONCLUSIONS

Modifying the kraft pulping process offers promise as a means of controlling the bleachability of kraft pulps. By modifying the pulping process, it is possible to alter the nature of residual lignin and this can impact chlorine dioxide delignification chemistry. The results of these studies suggest that condensed phenolics contribute to the overall bleachability of kraft pulps. Before a complete description of pulp bleachability can be provided other factors including the role of lignin-carbohydrate complexes need to be investigated.

## ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of K. Crofut at Ahlstrom Machinery in Glens Falls, NY, for performing the pulping studies and B. Broerman at Union Camp Corp. for providing the investigators with wood supplies. The authors also wish to express their sincere appreciation to the U.S. Department of Energy (Cooperative Agreement DE-FC07-961D 13442) and the Member Companies of the Institute of Paper Science and Technology for their financial assistance for this project.

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**Goal 3:** This year's last research goal for our peroxide studies was to examine the bleachability of methylated kraft pulps with P and P* . The goal of these studies was to evaluate the importance of phenoxy groups for pressurized peroxide. To accomplish this goal we reacted a softwood kraft pulp with alkaline dimethylsulfate. Methoxy analysis of the pulp indicated that the starting pulp had a methoxy content of 1.2% (wt basis) and 1.9% after methylation. The methylated pulp and the initial brownstock were then treated to a P* and P-stage. Table 3 summarizes the bleaching conditions employed and results of the peroxide stages.

Table 3. Kappa number and klason lignin for softwood kraft pulp (methylated and non-methylated) before and after P and P*.

| | | **Peroxide Stage: 1% $H_2O_2$, 0.8% NaOH, 0.05%$MgSO_4$, 60 psi $O_2$, 2 hr** | | |
|---|---|---|---|---|
| | **Initial** | **70°C** | **90°C** | **110°C** |
| **Brownstock[1]: Kappa #** | 30.5 | 28.3 - 7% | 27.9 - 8% | 25.9 - 15% |
| **Methylated Pulp ; Kappa #** | 21.4 | 18.9 - 12% | 18.0 - 16% | 18.5 - 14% |
| **Brownstock: Klason** | 4.8 | 4.2 - 12% | 4.6 - 4% | 3.9 - 18% |
| **Methylated: Klason** | 5.7 | 5.0 - 12% | 5.1 - 10% | 4.8 - 16% |

[1]brownstock was alkaline extracted prior to P and P* conditions.

The results of the experiments in Table 3 were rather unexpected. The data suggests that the methylated pulp exhibited bleachability comparable to the unmethylated brownstock. Based on literature results and our prior experience, we had anticipated that low temperature peroxide delignification of methylated pulp would suffer decreased performance. For the pulps used in this study this was not observed. Currently, we are uncertain as to the precise factors contributing to this effect. One explanation may be that we had insufficient methylation of the pulp. Hence, this would allow for peroxide delignification to proceed especially when a low charge of peroxide is used. If this hypothesis is correct, it would imply that peroxide delignification requires only a limited amount of free phenolics to initiate delignification.

## Experimental

Materials. All pulps employed in these studies were acquired from commercial operations throughout North America. All chemicals, except $ClO_2$, were commercially purchased and used as received.

Residual Lignin Isolation. Brownstock pulps were extracted with acetone for 24 hours in a Soxhlet extractor, washed thoroughly with de-ionized water, and air dried prior to isolating the residual lignin. The air dried pulp was placed in a round-bottom flask diluted with 0.10 N HCl 9:1 dioxane:water yielding a final consistency of 4%. After refluxing the pulp slurry for 1 h under argon, the mixture was cooled and filtered. The filtrate was neutralized with sodium bicarbonate, filtered, and worked-up following Gellerstedt and Lindfor method (Gellerstedt, G.; Lindfors, E. On the Structure and Reactivity of Residual Lignin in Kraft Pulp Fibers. *International Pulp Bleaching Conference Proceedings*, Stockholm, Sweden, SPCI, **1991**, *1*, 73-88 (1991)). Yields varied from 30-50%.

NMR Spectroscopy. All NMR spectra were recorded on a Bruker 400 MHz DMX NMR spectrometer.

$^1$H NMR Analysis of Residual Lignin. The lignin samples were dissolved in anhydrous DMSO-$d_6$. Sodium-3-trimethylsiyl propinate-2,2,3,3-$D_4$ was added as an internal standard and the samples were analyzed by NMR using a 400 MHz Bruker DMX spectrometer. The analyses were accomplished employing a $\pi/2$ pulse, 25-sec delay, 12,000 Hz sweep width, and 240 transients. The FID was fourier transformed with 1 Hz of line broadening and one degree of zero filling. Data analysis was accomplished using methods described in the 1997 spring PAC report.

Pulp methylation: To a 3% consistency pulp slurry (20 gr o.d.) was added dimethyl sulphate (26 ml) at a rate of approximately 0.1 ml/second from a burette. Concurrently, a 30% NaOH solution was added to the pulp slurry from another burette at approximately the same rate as dimethyl sulphate solution. The solution was maintained above pH 10 and stirred vigorously for 2 hours at room temperature. The pulp was then filtered, washed, dried and characterized.

## Future Recommendations

The use of peroxide in an EOP stage is one of the most practical technologies available to improve pulp bleaching while minimizing AOX discharges. The optimal relationship between the charge of chlorine dioxide in $D_0$ and peroxide in the subsequent EOP-stage is not well understood. Future studies will be directed at maximizing the brightening effects of these two chemicals. This will be accomplished by:

- Determining how the $D_0$ stage impacts bleachability in a EOP-stage;

- Evaluating how the chemistry of an EOP stage impacts reversion properties of a fully bleached pulp;
- Studying the lignin structural units predisposed to oxidation by an EOP-stage.

**Research Benefits**

The anticipated benefits of these studies include:

- New ECF-"lite" bleaching sequences;
- Improved properties of the final product;
- Reduced $ClO_2$ usage and chloride generation.

## Supporting Literature

Additional background information in the field of (EOP) chemistry can be found in the following articles:

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Proceedings (TAPPI): 131-138 (October,1997)

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Sharpe, P.; Rangamannar, G.
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Júnior, F.; Resende, A.
O Papel 58, no. 10: 46, 68-69, 72 (October,1997).

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Effects of D100 Filtrate Recycle on DEopD Bleach-Plant Performance
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## Influence of Hexenuronic Acids (HexA) on Bleaching *by Art J. Ragauskas*

### Summary of Past Results

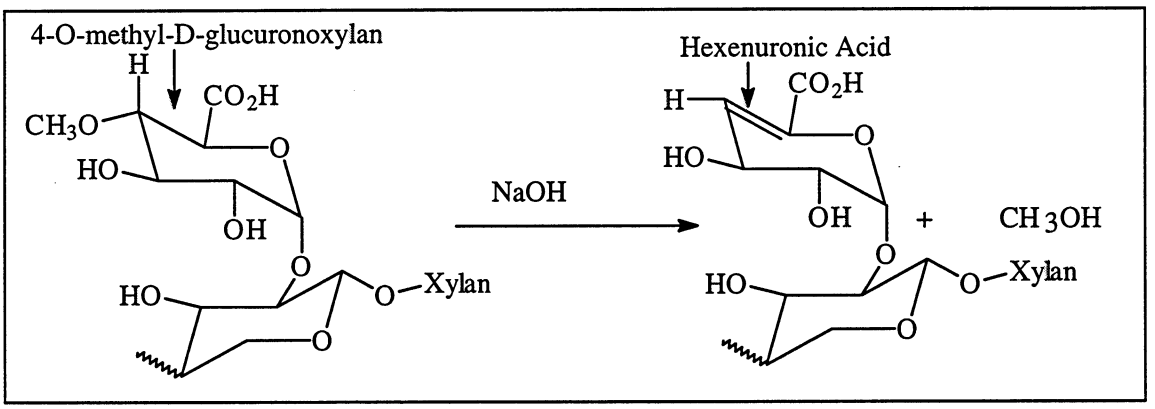
FY 1996-97 research efforts established that for low-kappa hardwood kraft pulps hexenuronic acids contribute approximately 50% to the apparent kappa number of the pulp. For softwood kraft pulps, the results were more variable, but it appeared that hexenuronic acids contribute approximately 0-15% of the total kappa number. The presence of hexenuronic acids was indirectly determined by employing an acid hydrolysis procedure, UV analyzing the effluents, and measuring the pulp kappa number before and after hydrolysis.

Metals analysis of kraft pulps before and after an acid treatment stage indicates a substantial drop in metals content for the post-treated pulps. These results suggest that hexenuronic acids may be involved in the overall metal affinity mechanism for kraft pulps. Preliminary bleaching studies indicate that the presence of hexenuronic acids in pulp results in the consumption of chlorine dioxide and ozone chemical. This loss of bleaching chemical could be avoided if the hexenuronic acids are removed with an acidic stage before bleaching.

### Hexenuronic Acids: Background

Hexenuronic acids are derived from 4-O-methyl-D-glucuronoxylan during the kraft pulping process (see Fig. 1). This reaction was proposed by Clayton (Svensk Papperstidning, Feb., p 115,1963) to explain the behavior of popular, birch and elm 4-O-methyl-D-glucuronoxylans under alkali at 170°C.

Figure 1: Alkali-catalyzed formation of hexenuronic acids.




A variety of investigators have studied this reaction since Clayton's report. Perhaps two of the most notable publications in this field are the reports by Vuorinen et al. (Conf. Proceedings from 1996 Int. Pulp Bleach. Conf., 1, p 43, 1996) and Buchert et al. (Tappi J., 78, p 125, 1995), which demonstrated that hexenuronic acids could be removed with a mild acid treatment and that if these sugars are not removed, they react with electrophilic

bleaching chemicals such as chlorine dioxide and ozone (Note: additional background material in this field is summarized at the end of the HexA report)

## Research Goals

FY 1997-98 goals for this section of F015 are listed below:

1. Explore the use of lower temperatures (<100°C) and mild pH conditions to remove hexenuronic acids in hardwood kraft pulps.

2. Determine the effects of hexenuronic acid removal on pulp yield, viscosity, strength, metal binding properties, and $ClO_2$ bleachability.

3. Determine the influence of AQ, polysulfide, and AQ/polysulfide have on hexenuronic acid generation during kraft pulping.

4. Study the effect of $O_2$ delignification on hexenuronic acids.

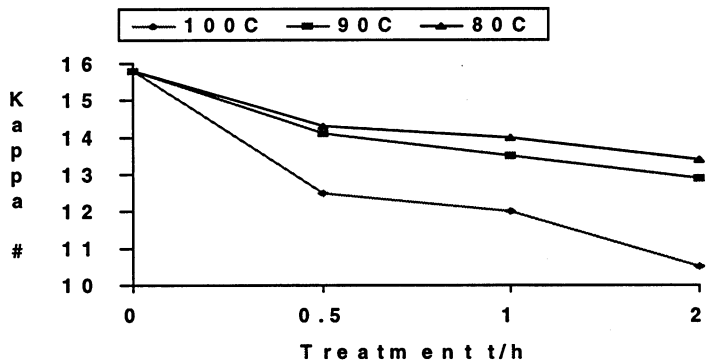
These research goals have been accomplished over this past fiscal year, and the results of these investigations are summarized in this report.

## Results

**Goals 1, 2, and 4:**

Effect of Temperature on HexA Removal: Past HexA studies have utilized a low consistency, hot (100°C) sodium formate/formic acid (pH 3) buffered solution to remove HexA from kraft pulps over a time period of 2 to 5 hr. This year,we began to explore the use of alternative HexA removal strategies. Our initial goal was to examine the effect of temperature on acid removal of HexA from a hardwood kraft pulp. Figure 2 summarizes the results of varying the temperature for HexA removal using our standard conditions (i.e., buffered pH 3.0 and 3% csc).

Figure 2: Change in kappa number for a HW kraft pulp treated with 10 mM sodium formate/formic acid at 80°, 90°, 100°C.




This study suggested that the HexA removal process is temperature sensitive and that the optimal temperature needs to be between 90° to 100°C. The 100°C experiments were

performed on a large scale so that yield measurements were experimentally feasible. The pulp yield after 2 hr of refluxing was 99.0%. When the hydrolysis procedure was performed at a pH of 7.0, our pulp yield was 98.6% suggesting that the acid hydrolysis procedure can be accomplished without significant loss of fiber. This conclusion is supported by examining the viscosity values for the kraft pulps treated with acid for two hr (see Table 1).

Table 1: Viscosity for hardwood kraft pulp pre- and post acid hydrolysis.

| Pulp | Viscosity/cP |
|---|---|
| Initial Brownstock | 40.0 |
| 2 h pH 3.0, 100°C | 34.8 |
| 2 h pH 3.0, 90°C | 33.8 |
| 2 h pH 3.0, 80°C | 33.8 |

Physical Strength Properties: Although the yield and viscosity data suggested nominal damage to the carbohydrates during the hot acid treatment stage, further investigations were required. To assess the impact of the hot acid treatment stage on physical properties, the pulp fibers were refluxed at pH 3 and 7 and were characterized for their physical strength properties. The results of these investigations are summarized in Table 2.

Table 2. Physical properties for hardwood kraft pulp (Initial kappa number: 15.8) refluxed in pH 3 and 7 water at 3% csc for 2 hr.

Pulp: HW kraft refluxed for 2 hr at pH 3.

| *PFI Revolutions* | *0* | *600* | *1000* | *1750* |
|---|---|---|---|---|
| CSF | 598 | 451 | 424 | 330 |
| Basis weight, g/m$^2$ | 64.43 | 65.07 | 65.52 | 66.28 |
| Caliper, microns | 137.7 | 119.9 | 109.1 | 101.8 |
| Density, g/cm$^3$ | .468 | .543 | .601 | .651 |
| Tear Index mN*m$^2$/g (Std. dev.) | 2.52 (.28) | 5.36 (.60) | 6.55 (.27) | 7.19 (.39) |
| Burst Index, kPa*m$^2$/g (Std. dev.) | 0.54 (.05) | 1.78 (.06) | 2.62 (.14) | 3.65 (.08) |
| Tensile Index, Nm/g (Std. dev.) | 13.19 (.87) | 32.21 (2.37) | 38.66 (1.80) | 48.80 (2.81) |
| Zero Span Tensile Index (Std. dev.) | 99 (10) | 118 (3) | 117 (7) | 122 (8) |

Table 2-*continued*

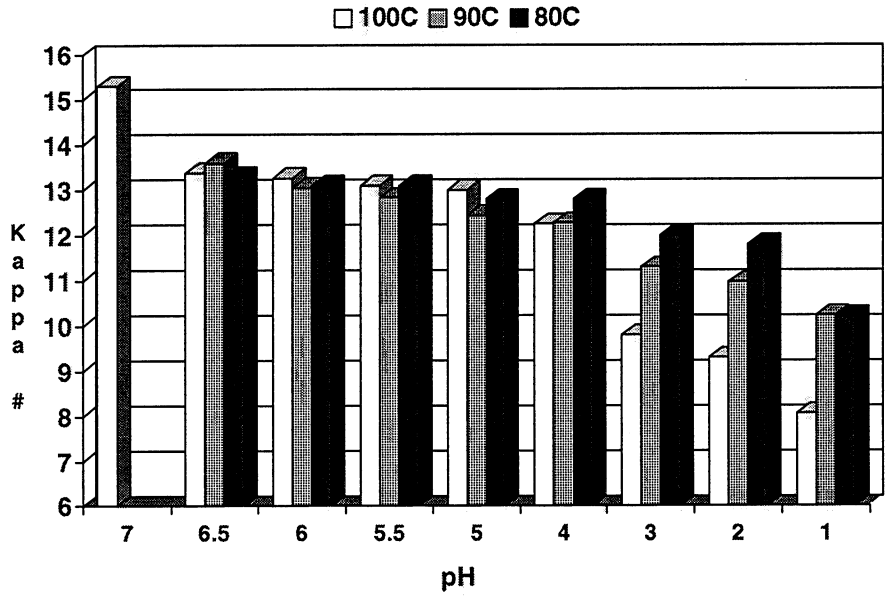
Pulp: HW kraft refluxed for 2 hr at pH 7.

| *PFI Revolutions* | *0* | *600* | *1000* | *1750* |
|---|---|---|---|---|
| CSF | 606 | 471 | 433 | 274 |
| Basis weight, g/m$^2$ | 66.19 | 66.55 | 66.19 | 65.46 |
| Caliper, microns | 137.3 | 117.4 | 108.5 | 97.2 |
| Density, g/cm$^3$ | 0.482 | 0.567 | .610 | .674 |
| Tear Index mN*m$^2$/g (Std. dev.) | 2.92 (.27) | 6.33 (.42) | 6.55 (.26) | 7.70 (.12) |
| Burst Index, kPa*m$^2$/g (Std. dev.) | 0.78 (.02) | 2.26 (.10) | 3.28 (.11) | 4.59 (.14) |
| Tensile Index, Nm/g (Std. dev.) | 18.66 (1.38) | 37.46 (2.92) | 50.03 (1.95) | 66.32 (3.10) |
| Zero Span Tensile Index (Std. dev.) | 92 (9) | 105(7) | 106(6) | 101 (10) |

The analysis of the zero span tensile data suggest that the hot-acid treatment may improve the intrinsic fiber properties. However, the lower tear, burst, and tensile index suggested decreased fiber bonding properties. These interpretations need to be supported by further paper testing investigations.

Alternative Acid for HexA Removal: To examine the possibility of removing HexA with a more practical acid, the hardwood kraft pulp (initial kappa number: 15.8) was placed in a 3% csc solution of sulfuric acid. The initial pH was varied from 6.5 to 1.0 and the pulp was kept in a constant water bath for two hr and then filtered and characterized. These analyses are summarized in Figure 3. This data, once again, suggests that temperatures near 100°C are optimal for HexA removal and the preferred initial pH range is near 3.

Figure 3: Effect of varying the initial pH on the acid hydrolysis[b] of hardwood kraft pulp.




[a]initial pH of the pulp solution was adjusted using 1N $H_2SO_4$: [b]pulp was treated with dilute sulfuric acid, sealed in a plastic bag, and immersed in a constant water bath for 2 hr; upon completion of the reaction, the pulp was well washed and kappa number was determined.

Metal Removal: Last year's HexA research clearly demonstrated that the acid hydrolysis procedure was removing significant amounts of non process elements (NPE), as was to be expected in light of modern day NPE pulp removal technologies. Nonetheless, the loss of NPEs seemed to be related to the magnitude of HexA removal during an acid treatment. To further explore this issue, several kraft pulps were acid-treated to remove HexA (standard hot acid treatment at pH 3 buffered conditions) and the metals content of the pulp was measured before and after the treatment. Furthermore, the metal binding capacity of the pre and post acid treated pulp was evaluated and this was shown to correlate with the content of HexA in the pulp. Figures 4 and 5 summarize the changes in metal content for a hardwood kraft pulp refluxed in sodium formate/formic acid solution for two hr. [Note: kappa number before and after treatment were 15.8 and 10.5(100°C), 12.9(90°C), 13.4(80°C), respectively.]

Figure 4: Changes in calcium content for a hardwood kraft pulp (initial kappa number:15.8) refluxed in pH 3 sodium formate/formic acid for 2 hr.

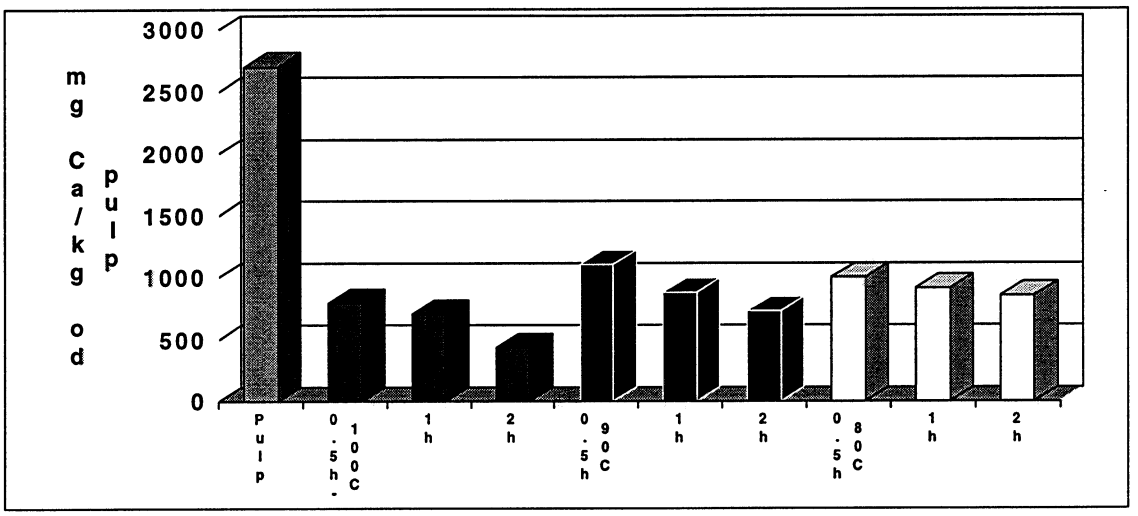
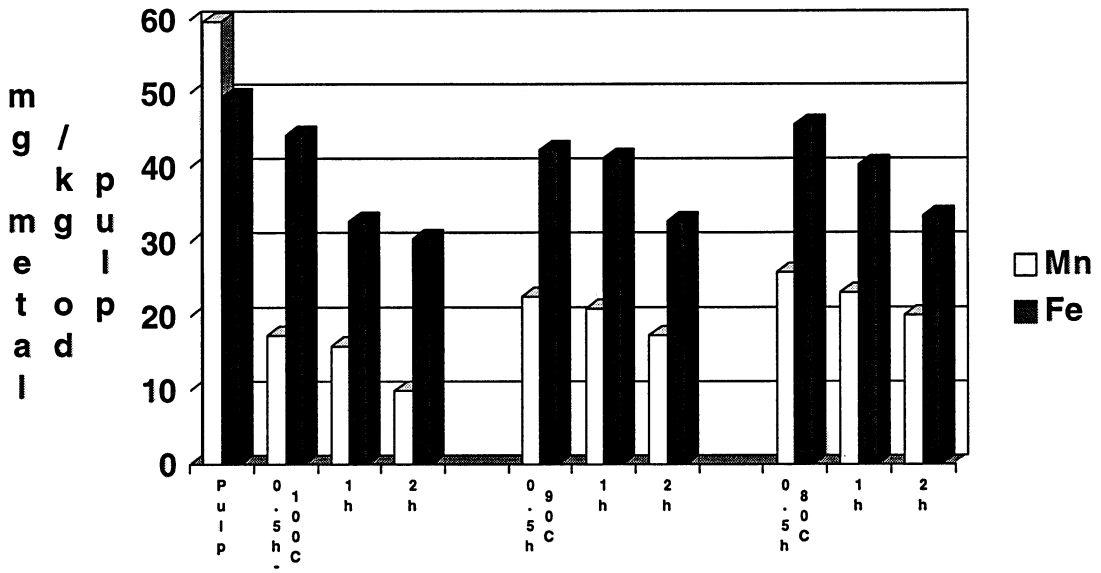



Figure 5: Changes in calcium content for a hardwood kraft pulp (initial kappa number: 15.8) refluxed in pH 3 sodium formate/formic acid for 2 hr.




It is interesting to note that the loss of Ca occurs rapidly during the first 30 min of an acid treatment, whereas the loss of Mn and Fe are slower, requiring additional time for their release from the pulp. As is expected, the release of metals is temperature-dependent and the results in Figures 4 and 5 suggest that higher temperatures favor NPE removal.

To further explore the generality of NPE removal, a series of maple and birch kraft pulps were treated with our standard acid hydrolysis conditions (i.e., reflux, pH 3, formic acid/sodium formate solution) and the change in NPEs and kappa number were

determined. These results are summarized in Table 3. For the hardwoods studied, the hot acid treatment decreased the initial kappa number by 14 - 50%. The decrease in NPE also varied significantly and appeared to be dependent on pulp and metal species.

Table 3. Changes in kappa number and NPE profile for a series of hardwood kraft pulps refluxed in pH 3 buffer for 5 hr.

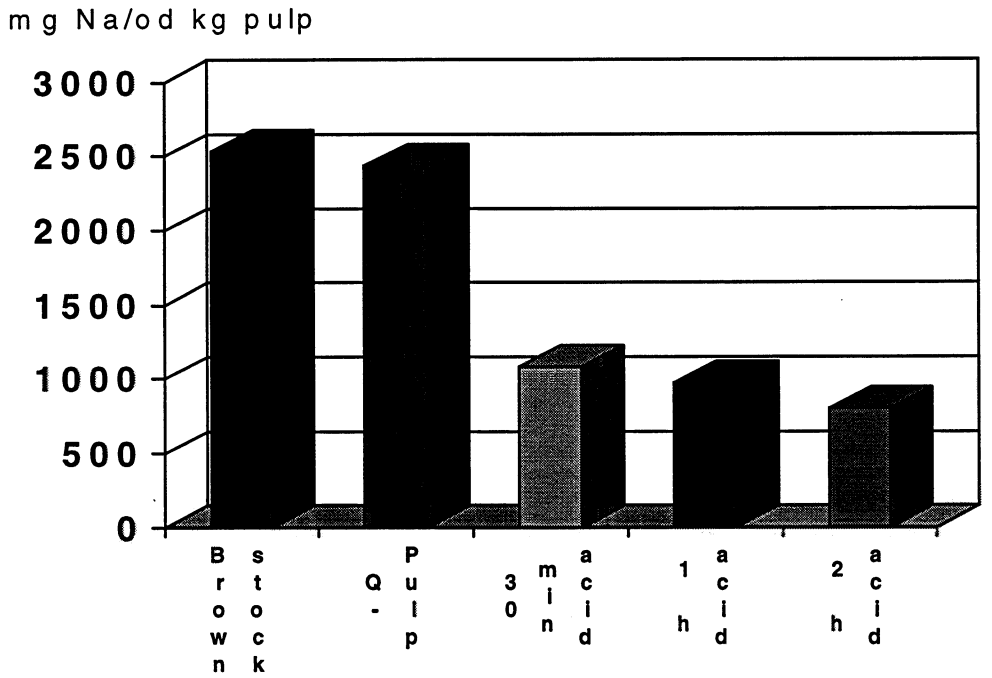
| Pulp | Kappa # | Na | Ca | Ba | K | Mg | Mn | Fe |
|---|---|---|---|---|---|---|---|---|
| Birch | | | | | | | | |
| initial | 28.1 | 1175 | 1795 | 7.46 | 57.5 | 279 | 6.9 | 49.6 |
| 5h | 24.3 | 71.1 | 527 | 3.06 | <6.02 | 69.5 | 2.0 | 48.4 |
| Birch | | | | | | | | |
| initial | 16.2 | 1735 | 1100 | 5.11 | 24.0 | 103.0 | 4.8 | 12.7 |
| 5h | 10.0 | 83.1 | 224 | 1.18 | 6.79 | 19.1 | 0.95 | 9.4 |
| Birch | | | | | | | | |
| initial | 14.7 | 56.7 | 2435 | 11.3 | 20.4 | 212.0 | 5.61 | 23.0 |
| 5h | 9.6 | 25.8 | 280 | 4.31 | 14.1 | 19.6 | 0.62 | 11.6 |
| Birch | | | | | | | | |
| initial | 13.9 | 49.8 | 1919 | 4.72 | 10.2 | 185.0 | 3.62 | 34.2 |
| 5h | 9.1 | 15.5 | 266 | 1.51 | <7.6 | 21.6 | 0.48 | 12.2 |
| Maple | | | | | | | | |
| initial | 23.8 | 1465 | 1345 | 8.01 | 25.8 | 173 | 25.5 | 226 |
| 5h | 15.0 | 52 | 380 | 3.44 | <9.3 | 33.8 | 7.5 | 218 |
| Maple | | | | | | | | |
| initial | 20.5 | 1360 | 920 | 9.15 | 22.1 | 150 | 31.4 | 248 |
| 5h | 13.9 | 33.8 | 374 | 2.53 | <10 | 38.2 | 7.8 | 232 |
| Maple | | | | | | | | |
| initial | 19.9 | 1320 | 721 | 7.0 | 15.0 | 127 | 32.1 | 12.5 |
| 5h | 15.1 | 37.6 | 185 | 2.2 | <5.9 | 21.3 | 4.6 | 8.9 |
| Maple | | | | | | | | |
| initial | 19.8 | 1480 | 1325 | 13.2 | 29.3 | 195 | 41.0 | 6.9 |
| 5h | 14.7 | 73.1 | 310 | 4.47 | 7.34 | 34.3 | 7.13 | 7.7 |
| Maple | | | | | | | | |
| initial | 18.7 | 1475 | 1285 | 9.14 | 61.2 | 205 | 34.9 | 44.5 |
| 5h | 13.0 | 104 | 308 | 3.55 | <9.8 | 40.5 | 8.5 | 52.0 |
| Maple | | | | | | | | |
| initial | 17.1 | 1260 | 1190 | 8.14 | 43.6 | 201 | 33.3 | 177 |
| 5h | 11.6 | 50.4 | 200 | 2.42 | 9.2 | 27.7 | 6.1 | 78.7 |
| Maple | | | | | | | | |
| initial | 16.2 | 68.7 | 1875 | 8.72 | 20.1 | 203 | 15.3 | 25.3 |
| 5h | 8.5 | 23.4 | 337 | 3.92 | 20.2 | 22 | 1.4 | 11.6 |
| Maple | | | | | | | | |
| initial | 14.5 | 347 | 1945 | 8.64 | 19.7 | 245 | 25.1 | 12.1 |
| 5h | 9.5 | 29.3 | 176 | 2.54 | <6.8 | 26.6 | 2.3 | 6.9 |
| Maple | | | | | | | | |
| initial | 14.1 | 775 | 775 | 12.2 | 26.1 | 128 | 24.3 | 12.7 |
| 5h | 8.5 | 42.1 | 110 | 3.46 | 8.2 | 16.4 | 2.9 | 7.5 |

Table 3. *continued*

| Pulp | Kappa # | Na | Ca | Ba | K | Mg | Mn | Fe |
|---|---|---|---|---|---|---|---|---|
| Maple | | | | | | | | |
| initial | 13.5 | 503 | 1360 | 8.33 | 37.5 | 246 | 25.7 | 16.6 |
| 5h | 7.6 | 26.8 | 205 | 1.63 | <7.9 | 24.1 | 2.07 | 16.0 |
| Maple | | | | | | | | |
| initial | 12.1 | 1760 | 1013 | 13.7 | 23.1 | 171 | 36.8 | 16.8 |
| 5h | 7.5 | 53.6 | 147 | 6.24 | <7.8 | 21 | 4.5 | 13.1 |
| Maple | | | | | | | | |
| initial | 12.0 | 43.2 | 1725 | 6.81 | 11.6 | 195 | 1.83 | 55.0 |
| 5h | 8.3 | 10.8 | 203 | 1.94 | 5.14 | 15 | | 26.5 |
| Maple | | | | | | | | |
| initial | 11.7 | 67.8 | 1780 | 8.54 | 19.2 | 200 | 9.68 | 10.5 |
| 5h | 7.0 | 16.9 | 250 | 5.17 | 11 | 17.8 | 0.91 | 5.6 |

To further investigate the NPE binding capacity of a HexA-free kraft pulp, we treated a hardwood kraft pulp to a routine EDTA Q-stage. The brownstock, chelated pulp, and hot acid-treated pulps (i.e., pH 3, 100°C) were immersed in a 1 N NaCl solution overnight. The resulting pulps were washed with deionized water and analyzed for metals analysis. The results of this analysis are summarized in Figure 6.

Figure 6: Total sodium content of hardwood kraft pulps [brownstock, EDTA-chelated, hot acid treated(½, 1, and 2 hr)] after immersion in 1.0 N NaCl for 16 hr.




These results suggest that not only does a hot acid stage remove metals, but it also eliminates the binding sites in the pulp. In summary, future studies into pulp binding

properties of NPE must take into account the role of hexenuronic acids. The removal of HexA provides a viable solution to the control of NPE in a closed mill operation.

Behavior of post-oxygen delignified kraft pulp to hot acid stage.

Upon the recommendation of the fall 1997 PAC a post-oxygen delignified hardwood kraft pulp was treated with a hot acid stage and the resulting pulp and effluent were analyzed (see Table 4).

Table 4. Analysis of pulp and effluent properties after a hot acid treatment.[1]

| Pulp | Kappa # | HexA in Effluent |
|---|---|---|
| Commercial HW kraft pulp post-$O_2$ | 9.4 | -- |
| Commercial HW kraft pulp post-$O_2$ hot acid treatment for ½ h | 7.1 | 0.43 mM |
| Commercial HW kraft pulp post-$O_2$ hot acid treatment for 1 h | 6.2 | 0.82 mM |
| Commercial HW kraft pulp post-$O_2$ hot acid treatment for 2 h | 5.2 | 1.18 mM |

[1]hot acid was performed at pH 3 at 100°C.

Along with the changes in kappa number, we also characterized the changes in metals content for the starting pulp and the hot acid treated pulps. (see Table 5). The metal binding capacity of the pulps described in Table 5 were evaluated by immersing each pulp in a 1N NaCl solution overnight. The resulting pulps were filtered, washed with deionizied water, and examined for sodium content. The results of these studies are summarized in Table 6. This data demonstrate that a hot acid stage removes both NPE from the pulp and the metal binding site in the pulp.

Table 5. Changes in metals content for oxygen delignified HW kraft pulp before and after hot acid treatment.

| Pulp | Ba(mg/kg od pulp) | Ca | Fe | K | Mg | Mn | Na |
|---|---|---|---|---|---|---|---|
| $O_2$ HW Kraft DI washed | 51.4 | 3050 | 7.56 | 109 | 236 | 66.4 | 871 |
| $O_2$ HW kraft ½ hr hot acid stage | 15.9 | 876 | 5.03 | 9.52 | 54.5 | 19.8 | 61.9 |
| $O_2$ HW kraft 1hr hot acid stage | 12.4 | 721 | 3.93 | 7.82 | 42.3 | 15.9 | 75.7 |
| $O_2$ HW kraft 2hr hot acid stage | 11.2 | 583 | 4.14 | 5.65 | 34.9 | 12.6 | 37.9 |

Table 6. Amounts of sodium present in $O_2$ HW kraft pulps after immersion in 1.0 N NaCl solution overnight.

| Pulp | Na(mg/kg od pulp) |
|---|---|
| $O_2$ HW Kraft DI washed | 1950 |
| $O_2$ HW Kraft EDTA Chelated | 1990 |
| $O_2$ HW kraft ½ hr hot acid stage | 1250 |
| $O_2$ HW kraft 1 hr hot acid stage | 1030 |
| $O_2$ HW kraft 2 hr hot acid stage | 844 |

Impact of HexA Removal on Bleachability: The PAC advisory group had recommended that the effects of HexA removal on pulp bleachability be examined this fiscal year. To achieve this goal, two hardwood kraft pulps were hot acid treated for 2 hr. The initial pulps and the HexA-free pulps were bleached with chlorine dioxide under typical Do conditions using a fixed charge of chlorine dioxide. The pulps were subsequently extracted. To determine if the HexA-free pulp had to be washed after the hot acid stage, the D stage was repeated using the effluent from the hot acid stage. The results of these studies are summarized in Tables 7 and 8.

Table 7. Effects of HexA removal on chlorine dioxide bleaching of a HW kraft pulp kappa number 15.8.

| Pulp | Kappa number | Viscosity/cP |
|---|---|---|
| HW Kraft-A Brownstock | 15.8 | 29.0 |
| HW Kraft-A Refluxed at pH 7 for 2 h | 14.7 | 26.7 |
| HW Kraft-A Refluxed at pH 7, Bleached DE[1] (1.12 % $ClO_2$) | 4.6 | 22.9 |
| HW Kraft-A Refluxed at pH 3 for 2 h | 10.7 | 27.5 |
| HW Kraft-A Refluxed at pH 3, Bleached DE[1] (0.813 % $ClO_2$) | 2.8 | 22.7 |

[1]all D stages were performed in sealed plastic bags at 10% csc, 50°C for 30 min., terminal pH: 3(for pulp refluxed at pH 7); 2.26(for pulp refluxed at pH 3); E-stage was at 10% csc, 1.4% NaOH (for pulp refluxed pH 7); 0.16% NaOH (for pulp refluxed pH 3) 70°C for 60 min.

Table 8. Effects of HexA removal (3 h hot acid stage) on chlorine dioxide bleaching of a HW kraft pulp kappa with and without washing after the hot acid stage.

| | Hardwood Kraft Pulp | HexA Removed Washed Kraft Pulp | HexA Removed Kraft Pulp Effluent Retained |
|---|---|---|---|
| Brownstock | 13.9 | 8.7 | -- |
| DE[a] - 1.2% $ClO_2$ | 6.3 | 3.2 | 3.2 |
| DE - 0.8% $ClO_2$ | 5.0 | 2.7 | 2.5 |

[1]all D stages were performed in sealed plastic bags at 10% csc, 50°C for 30 min.; E-stage was at 10% csc, 2.0% NaOH, 70°C for 120 min.

The results of these studies clearly demonstrate the benefits of removing HexA prior to a $D_0$ stage. Furthermore, the data in Table 8 indicate that pulp washing is not required after the hot acid stage.

**Goal 3.** Determine the influence of AQ, polysulfide and AQ/polysulfide have on hexenuronic acid generation during kraft pulping.

To investigate the effects of AQ on hexenuronic acid formation during kraft pulping, a series of conventional and AQ hardwood kraft pulps were acquired and treated with a hot acid stage. The kappa number of the pulps was determined before treatment and after 2 and 5 h of reflux in a pH 3 buffered solution. The results of these investigations are summarized in Figures 7 and 8. An examination of these data suggests that at any given kappa number, the pulp prepared with AQ will usually respond more favorably to a hot acid treatment (i.e., the AQ pulps has a greater drop in kappa number upon treatment with acid). These results suggest that a conventional pulp has more lignin and less HexA than an AQ kraft pulp at the same kappa number.

Figure 7. Changes in kappa number for conventional, and AQ HW kraft pulps treated to a 2 and 5 hr hot acid stage buffered at pH 3.

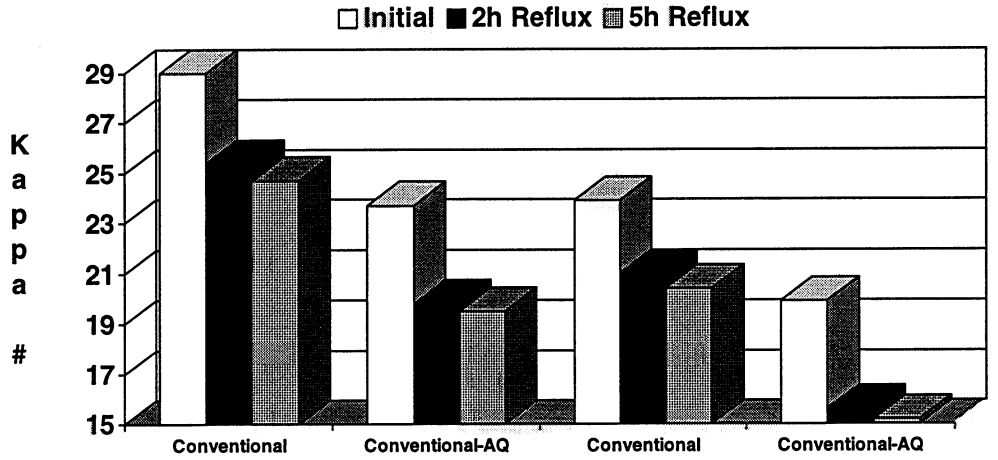
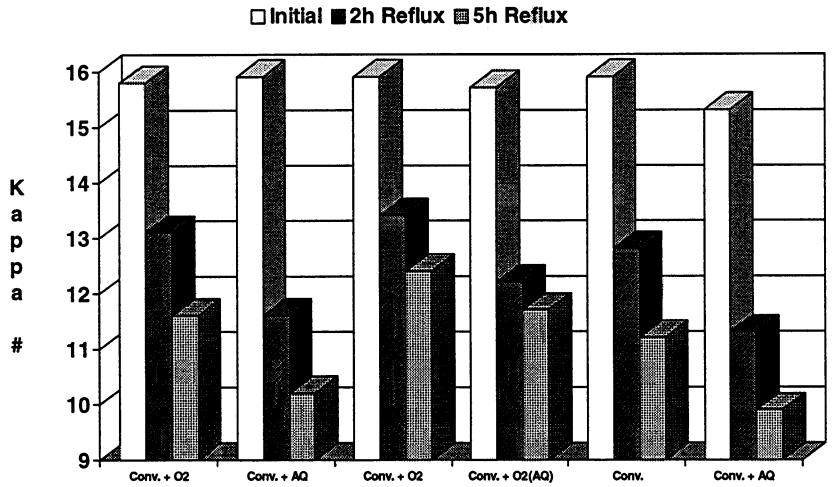



Figure 8. Changes in kappa number for conventional, AQ, conventional-$O_2$ delignified HW kraft pulps treated to a 2 and 5 h hot acid stage buffered at pH 3.



To explore the role of polysulfide/AQ in hexenuronic acid formation during kraft pulping, a series of conventional and polysulfide/AQ hardwood kraft pulps were acquired, hot acid treated, and analyzed. Tables 9 and 10 highlight the results of this studies.

Table 9. Physical properties of conventional and polysulfide/AQ hardwood kraft lab prepared pulps.

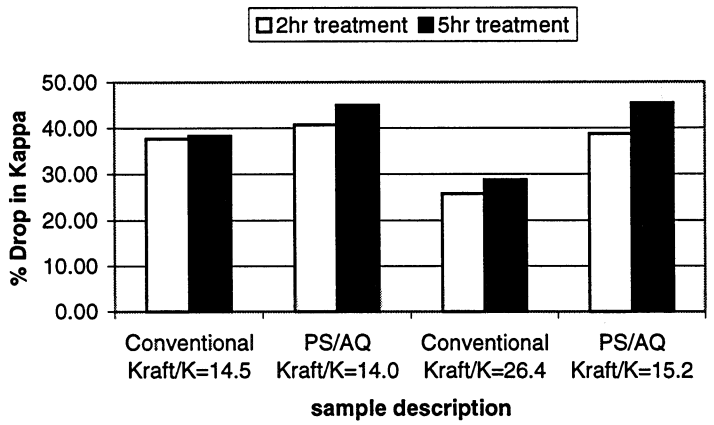
| Pulp | Kappa number | Carbohydrate Composition | | | |
|---|---|---|---|---|---|
| | | Glucan | Xylan | Arabinan | Mannan |
| Conventional Kraft | 14.6 | 67.5 | 18.2 | 0.45 | 1.42 |
| Conventional Kraft | 26.4 | 63.4 | 18.2 | 0.09 | 1.28 |
| Polysulfide/AQ | 14.0 | 67.1 | 19.2 | 0.45 | 1.03 |
| Polysulfide/AQ | 15.2 | 63.1 | 18.0 | 0.00 | 1.39 |

Table 10. Changes in kappa number and viscosity for conventional and polysulfide/AQ hardwood kraft pulps after 2 and 5 hr of hot acid treatment.

| Pulp | Initial Kappa number | Initial Viscosity/cP | Kappa number after 2 hr hot acid-stage | Kappa number after 5 hr hot acid-stage | Viscosity/cP after 5 hr hot acid-stage |
|---|---|---|---|---|---|
| **Conventional Kraft** | 14.6 | 36.5 | 9.1 | 9.0 | 37.0 |
| | | | | | |
| **PS/AQ -low polysulfide** | 14.0 | 29.9 | 8.3 | 7.7 | 27.0 |
| **Conventional Kraft** | 26.4 | 51.1 | 19.6 | 18.8 | 37.1 |
| **PS/AQ -high polysulfide** | 15.2 | 33.6 | 9.3 | 8.3 | 26.7 |

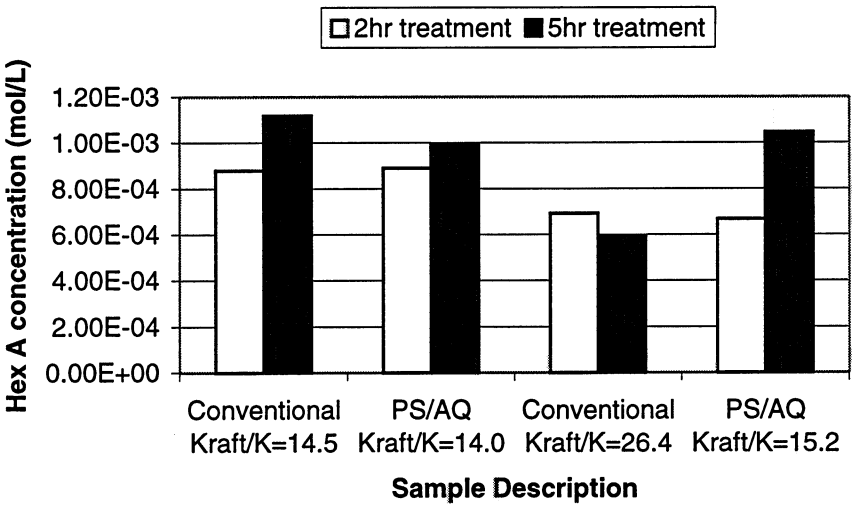
The data in Table 10 suggest that the polysulfide/AQ pulps have a slight enrichment in hexenuronic acids that could be attributed to the AQ. Figure 9 summarizes the % changes in kappa number after a 2 and 5 hr hot acid stage. These results suggest that the polysulfide does not decrease the amounts of HexA present in a pulp.

Figure 9. Relative decreases in kappa number for conventional and PS/AQ hardwood kraft pulps (see Table 5) treated to a hot acid stage.



This conclusion is also supported by the UV-analysis of the effluents of the hot acid stage. As described in the previous spring PAC report, UV analysis of the effluents from the hot acid stage provides an indirect measurement of hexenuronic acids in pulp. Figure 10 summarizes our UV-studies of the hot acid stage effluents for the conventional and PS/AQ kraft pulps described in Table 9.

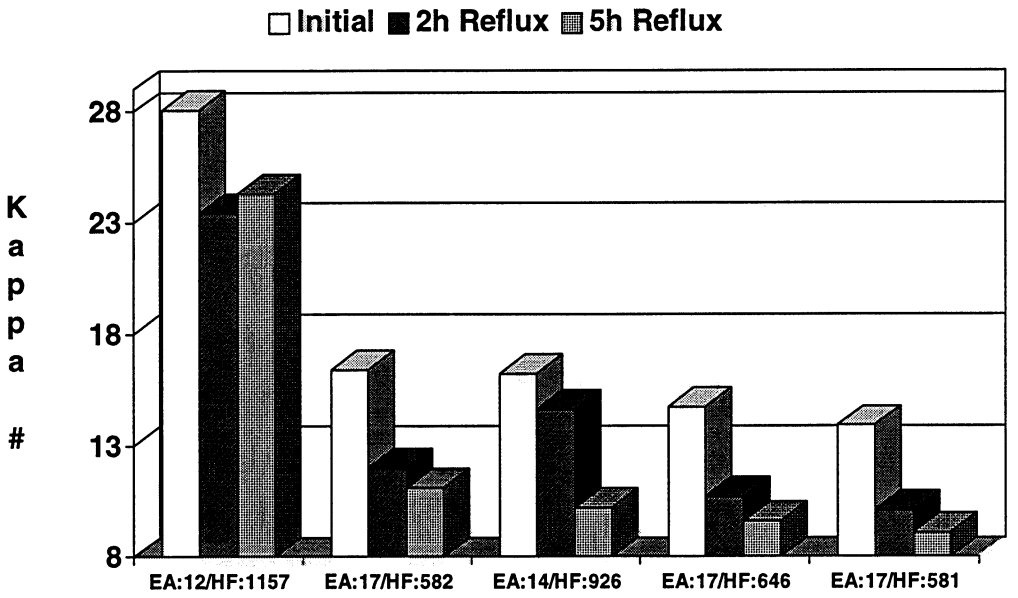
Figure 10. Amounts of "HexA" released during hot acid treatment of conventional and PS/AQ hardwood kraft pulps (see Table 5).




## Supplemental Studies:

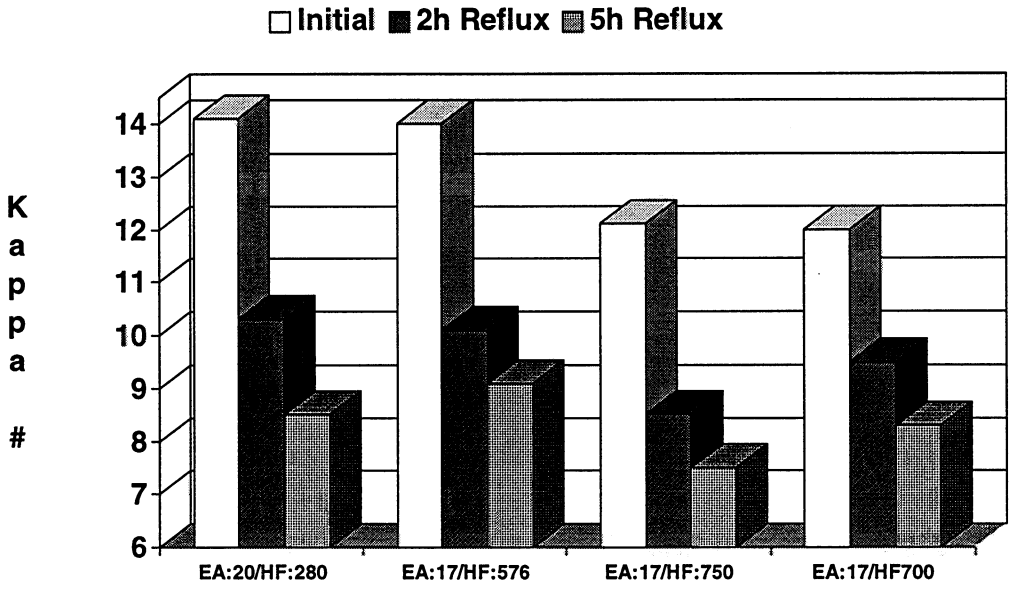
In addition to addressing all the goals of this subtask, we were able to begin exploratory studies directed at evaluating the effect of effective alkali (EA) and H-factor on the formation of hexenuronic acids. A series of birch and maple kraft pulps were subjected to a hot acid stage (i.e., 100°C buffered pH 3) for 2 and 5 hr. Each of these samples was then analyzed for kappa number. These results are summarized in Figures 11 and 12. An analysis of the birch data suggests that for pulps at equal kappa number, the pulp prepared with a higher EA will have a higher amount of hexenuronic acids (Note: this also suggest that less lignin is present). The same trend was also noted for the maple pulps. In addition, for pulps prepared with the same EA value but cooked to differing H-factor, the larger the H-factor the more HexA are present in the fiber. These conclusions need to be further validated. This will be explored in the next fiscal year.

Figure 11. Changes in kappa number for a series of conventional birch kraft pulps treated to a hot acid stage for 2 and 5 h.



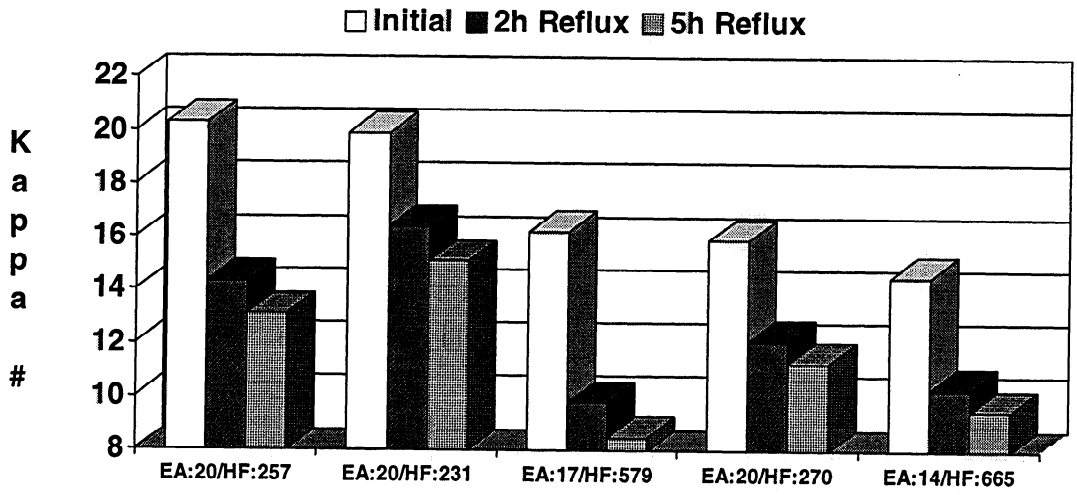

Note: Effective alkali (EA) and H-factor (HF) employed for each pulp is listed below each pulp sample.

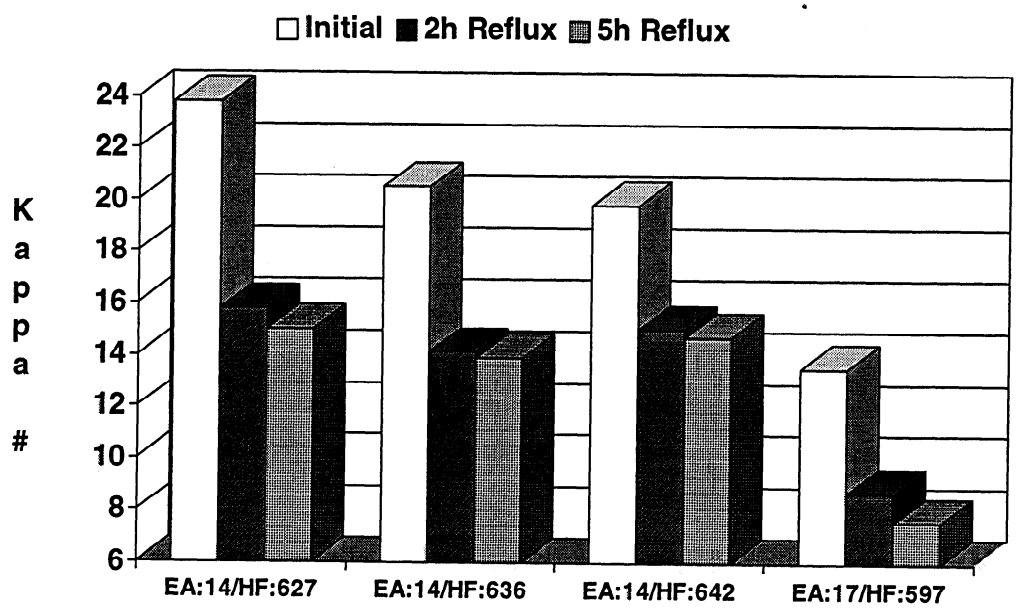
Figure 12: Changes in kappa number for a series of conventional maple kraft pulps treated to a hot acid stage for 2 and 5 h.




Note: Effective alkali (EA) and H-factor (HF) employed for each pulp is listed below each pulp sample.

Figure 12 -continued.



## Experimental

Materials: The maple and birch kraft pulps studied in this paper were prepared at IPST. The AQ, polysulfide/AQ, and control cooks described in Goal section 3 were lab pulps donated to this program. All other hardwood kraft pulps were acquired from commercial pulping operations throughout North America.

Acid Hydrolysis: A 3% consistency solution of a well-washed kraft pulp, 8.0 mM formic acid, and 2.0 mM sodium formate was rapidly warmed to a selected temperature (80°, 90° or 100°C) under argon. Pulp aliquots were removed, washed, and analyzed for kappa number. The acid effluents were analyzed by UV for 2-furoic acid following the Vuorinen's procedure (Conf. Proceedings from 1996 Int. Pulp Bleaching Conf., 1, p43, 1996).

Analytical Methods: Kappa number and viscosity determinations were performed in accordance with standard TAPPI procedures. Metals analysis was determined by ICP emission spectroscopy.

## Future Recommendations

Having established the relevancy of hexenuronic acids to hardwood kraft bleaching operations and adopted a quick analytical tool to detect these unsaturated sugars, several research opportunities are available, including:

Control of Hexenuronic Acids (HA) During Pulping:

- Determine the rate of (HA) formation during pulping;

Bleaching Chemistry of Hexenuronic Acids:

- Are HexA enriched pulps more bleachable?
- Can a Do stage effluent destroy HexA.

The goal of these proposed studies would be to develop the fundamental knowledge about hexenuronic acids so that their formation and/or bleaching impact could be minimized.

## Research Benefits

The anticipated benefits of these studies include:

- Reduced bleaching costs;
- Reduced generation of oxalic acid, facilitating mill closure;
- Improved mill operations.

## Supporting Literature

Additional background information in the field of hexenuronic acids can be found in the following articles:

Pulp Producers: Losing Metal or Resolve?
Lockie, M.
Pulp and Paper International 39, no. 10: 44, 46 (October 1997).

Nature of Organic Bound Chlorine from ECF Bleaching Found in Kraft Pulp
Törngren, A.; Gellerstedt, G.
9th International Symposium on Wood and Pulping Chemistry: 1997: Oral Presentations: M2-1-M2-4 (June 12, 1997).

Characterization of Uronic Acids During Kraft and Super Batch Pulping
Buchert, J.; Laine, J.; Tenkanen, M.; Vuorinen, T.; Viikari, L.
9th International Symposium on Wood and Pulping Chemistry: 1997: Oral Presentations: M3-1-M3-3 (June 12, 1997).

Selective Hydrolysis of Hexenuronic Acid Groups Opens New Possibilities for Development of Bleaching Processes
Vuorinen, T.; Fagerström, P.; Räsänen, E.; Vikkula, A.; Henricson, K.; Teleman, A.
9th International Symposium on Wood and Pulping Chemistry: 1997: Oral Presentations: M4-1-M4-4 (June 12, 1997).

Processes Which Metals Will Come to Dread [Are Based on Selective Acid Hydrolysis]
Roberts, J.
Pulp & Paper Europe 2, no. 5: 20-23 (June 1997).

Latest Breakthroughs in Chemical Pulp Bleaching
Pikka, O.; Vilpponen, A.
Paper Southern Africa 17, no. 2: 18-20, 22-24 (March/April 1997).

Latest Breakthroughs in Chemical Pulp Bleaching
Hanninen, E.; Pikka, O.; Vilpponen, A.
51st Appita Annual General Conference, 1997, 1: Proceedings, Paper no. 2A43: 269-275 (1997).

Effects of Pulping and Bleaching on Pulp Carbohydrates and Technical Properties
Buchert, J.; Tenkanen, M.; Ek, M.; Teleman, A.; Viikari, L.; Vuorinen, T.
1996 International Pulp Bleaching Conference: Proceedings: 39-42 (April 14, 1996).

Selective Hydrolysis of Hexenuronic Acid Groups and Its Application in ECF and TCF Bleaching of Kraft Pulps
Vuorinen, T.; Buchert, J.; Teleman, A.; Tenkanen, M.; Fagerström, P.
1996 International Pulp Bleaching Conference: Proceedings: 43-52 (April 14, 1996).

Method of Treating Cellulose Pulps
Vuorinen, T.; Buchert, J.; Teleman, A.; Tenkanen, M.
Can. pat. 2,160,430. Issued April 14, 1996. 13 claims. 30 p. Cl.D21C9/00. Filed: Can. appln. 2,160,430 (October 12, 1995). Priority: Finn. appln. 4,808/94 (Oct.13, 1994).

Effects of Pulping and Bleaching on the Surface Composition of Kraft Pulps
Buchert, J.; Teleman, A.; Carlsson, G.; Tenkanen, M.; Laine, J.; Harjunpää, V.; Hausalo, T.; Viikari, L.; Ström, G.; Vuorinen, T.
8th International Symposium on Wood and Pulping Chemistry, June 6-9, 1995, Helsinki, Finland: Proceedings, 1: Oral Presentations: 567-573 (1995).

Identification of the Acidic Degradation Products of Hexenuronic Acid by NMR Spectroscopy
Teleman, A.; Hausalo, T.; Tenkanen, M.; Vuorinen, T.
8th International Symposium on Wood and Pulping Chemistry, June 6-9, 1995, Helsinki, Finland: Proceedings, 3: Poster Presentations: 109-114 (1995).

Use of Enzymes in Combination with Anion Exchange Chromatography in the Analysis of Carbohydrate Composition of Kraft Pulps
Tenkanen, M.; Hausalo, T.; Siika-aho, M.; Buchert, J.; Viikari, L.
8th International Symposium on Wood and Pulping Chemistry, June 6-9, 1995, Helsinki, Finland: Proceedings, 3: Poster Presentations: 189-194 (1995).

Structure of Hemicelluloses in Pine [Pinus] Kraft Cooking Liquors
Engström, N.; Vikkula, A.; Teleman, A.; Vuorinen, T.
8th International Symposium on Wood and Pulping Chemistry, June 6-9, 1995, Helsinki, Finland: Proceedings, 3: Poster Presentations: 195-200 (1995).

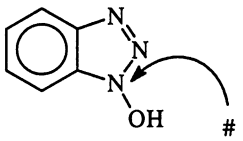
Effect of Cooking and Bleaching on the Surface Chemistry of Conventional Pine [Pinus] Kraft Pulp
Buchert, J.; Teleman, A.; Harjunpää, V.; Tenkanen, M.; Viikari, L.; Vuorinen, T.
Third European Workshop on Lignocellulosics and Pulp: Advances in Totally Chlorine-Free Bleaching Chemistry-Structure and Reactivity of Wood Components, Session Ultrastructure and Reactivity of Wood Fibers: 16-19 (Aug. 31, 1994).

## Laccase-Mediator Bleaching of Kraft Pulp *by Art J. Ragauskas*

### Summary of Past Results

The long-term research goal of this sub-project is to develop new enzymatic technologies which will improve kraft pulping and bleaching operations. Over the past three years, our research studies have focused primarily on laccase delignification chemistry to address these issues.

Our prior studies in this field have been directed at understanding the biobleaching chemistry of laccase and N-hydroxybenzotriazole.




# 1 Nitrogen position

N-hydroxybenzotriazole:NHB

We have shown that kraft pulps bleached with laccase/N-hydroxybenzotriazole were enriched in nitrogen. Caustic extraction was found to remove some of these nitrogen-containing materials, but not all of this extraneous material could be extracted. Although we were unable to definitely establish if the nitrogen in the pulp was due to the mediator and/or the laccase, we were able to determine that 99% of the mediator material could be recovered, suggesting that the incorporation of nitrogen into the pulp was due to the enzyme. A structural reactivity relationship of N-hydroxybenzotriazole demonstrated that it was absolutely critical for the hydroxy group of the mediator to be directly attached to N-1 of the triazole ring. Furthermore, we observed that the placement of electron-withdrawing groups on the aromatic ring was detrimental toward the biobleaching effect. Attachment of an electron-donating group onto the aromatic ring of the mediator also decreased the delignification capabilities of the laccase/mediator system.

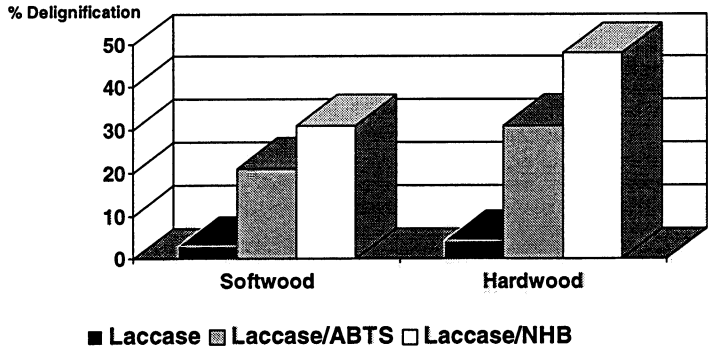
Studies directed at the fate of the mediator during a laccase/N-hydroxybenzotriazole stage demonstrated that the mediator was being converted into benzotriazole. This latter species was shown to be ineffective as a mediator for laccase. This loss of mediator was shown to be a rate limiting step for delignification of kraft pulps by laccase/N-hydroxybenzotriazole.

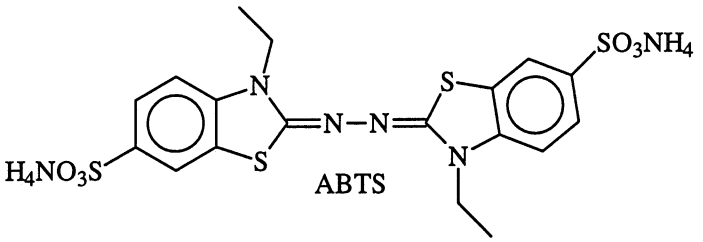
### Laccase Mediator Bleaching: Background

Recently, laccase mediator biobleaching have garnered increasing attention as researchers have improved the delignification properties of this enzymatic process. Although it was known for some time that laccase could degrade lignin-like structures, (T. Higuchi, Wood Sci. Technol., 24, 23(1990)) its application for delignifying kraft pulps was unsuccessful since the enzyme could not diffuse into pulp fibers due to size constraints. (L. Jurasek, J. Pulp Paper Sci., 21(8), J274(1995).) The first true breakthrough in this field came about when Bourbonnais and Paice (R. Bourbonnais and M. Paice, Appl. Microb. Biotech., 36,

823(1992) ) demonstrated that the addition of ABTS (2,2'azino-bis(3-ethylbenzo-thiazoline-6-sulphonic acid) to laccase resulted in substantial delignification of kraft pulps after an alkaline extraction stage. Representative delignification data acquired in our laboratories for laccase and laccase/ABTS are summarized in Figure 1.

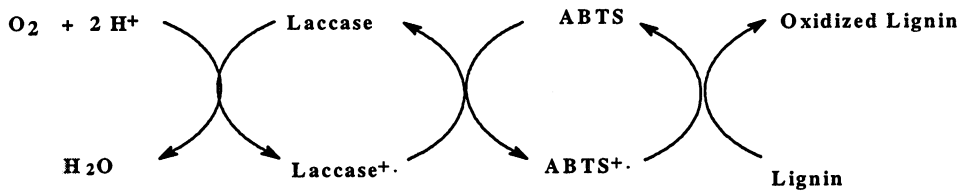
Figure 1. Delignification of softwood and hardwood kraft pulps by laccase, laccase/ABTS, and laccase/N-hydroxybenzotriazole.




This discovery initiated a flurry of fundamental research studies into the mechanism of ABTS/laccase bleaching. (A. Muheim, A. Fiechter, P. Harvery, and E. Schoemaker, Holzforschung, 46(2),121 (1992); M. Paice, I. Reid, R. Bourbonnais, F. Archibald, and L. Jurasek, Appl. Environ. Microb., 59(1), 260 (1993)) The results of these studies led to the suggestion that the mechanism of delignification for laccase/ABTS is based on a series of connective oxidative reactions, as summarized in Figure 2. The exact role of ABTS in the delignification process remains controversial, as Potthast et al. (A. Potthast, T. Roseneau, C.L. Chen, and J.S. Gratzl, J. Org. Chem., 60, 4320(1995).) and Fiechter et al. (A. Fiechter, P.J. Harvey, A. Muheim, and H.E. Schoemaker, Holzforschung, 46(2), 121(1992)) have suggested that the laccase-ABTS system does not generate a radical cation, and recently, Bourbonnais et al. (R. Bourbonnais, M. Paice, D. Leech, and B. Freiermuth, Conference Proceedings Biological Sciences Symposium, San Francisco, October, 335(1997)) proposed that the true delignification agent is the dication of ABTS.

Figure 2. Proposed laccase/ABTS delignification mechanism.




Recently, Call (H. Call, Conference Proceedings, TAPPI Emerging Pulping and Bleaching Technology Workshop, Durham, NC, 15(1995)) identified a new mediator, N-hydroxybenzotriazole, that exhibited improved bleaching performance. Figure 1 provides a comparative illustration of the bleaching capabilities of ABTS and N-hydroxybenzotriazole (NHB) with laccase followed by an alkaline extraction stage. Since this initial discovery, our research group (J. Sealey and A.J. Ragauskas, Fourth European Workshop on Lignocellulosics and Pulp, Stresa, Italy, September, 171(1996)) and others (M. Niku-Paavola, K. Poppius-Levlin, M. Ranua, L. Viikari, and W. Wang, Conference Proceedings, 1997 Biological Sciences Symposium, San Francisco, CA, 327(1997); H. Bermek, K. Eriksson, K. Li, Conference Proceedings, 1997 Biological Sciences Symposium, San Francisco, CA, 349(1997); D. Argyropoulos and C. Crestini, Conference Proceedings, 9th International Symposium on Wood and Pulping Chemistry, Montreal, Canada, June, 20(1997)) have been actively involved in studying the fundamental biobleaching principles involved in this delignification system. Recently, we determined that N-hydroxybenzotriazole was not stable under the bleaching conditions employed and this was reported at the 1996 spring PAC meeting. (Note: additional background material in this field is summarized at the end of the laccase report). Future advances in laccase biobleaching will require the development of new improved mediators.

## Research Goals

FY 1997-98 goals for this section of F015 are listed below:

1. Examine the use of laccase to reduce AOX in Do(EOP) effluents.

2. Determine the effects of laccase/N-hydroxybenzotriazole bleaching of kraft pulps with respect to yield, strength, and $ClO_2$ bleachability.

3. Examine the delignification capabilities of a laccase-mediator bleaching system with methylated kraft pulps.

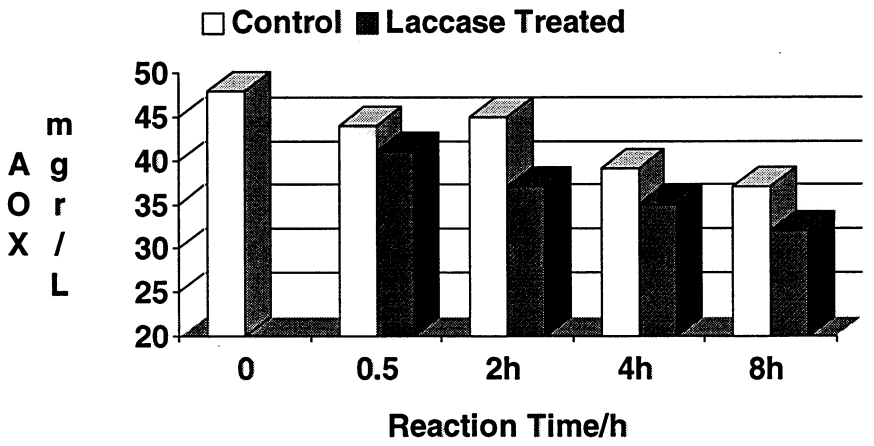
4. Study the application of a laccase/mediator system on high kappa kraft pulps.

These research goals have been accomplished over this past fiscal year and the results of these investigations are summarized in this report.

## Results

**Goal 1 :** Based on literature precedent and PAC interest, we examined the effects of laccase on AOX concentration in bleach plant effluent. A lab prepared D(EOP) effluent, generated from bleaching a softwood kraft pulp, was treated with laccase (29,200 U laccase/ml of effluent) at pH 4.5, 50°C for varying periods of time. A series of control experiments were also performed that replicated the laccase studies except that enzyme was not added. The effluents from these experiments were analyzed for AOX and the results are summarized in Figure 3.

Figure 3. Changes in AOX for a D(EOP) effluent treated with and without laccase at pH 4.5, 50°C at various times.



This data suggests that laccase treatment of bleach effluents can reduce AOX by 10-15%. In light of the recently proposed Cluster rules and the marginal decrease in AOX upon treatment with laccase, no further investigations were performed on this sub task.

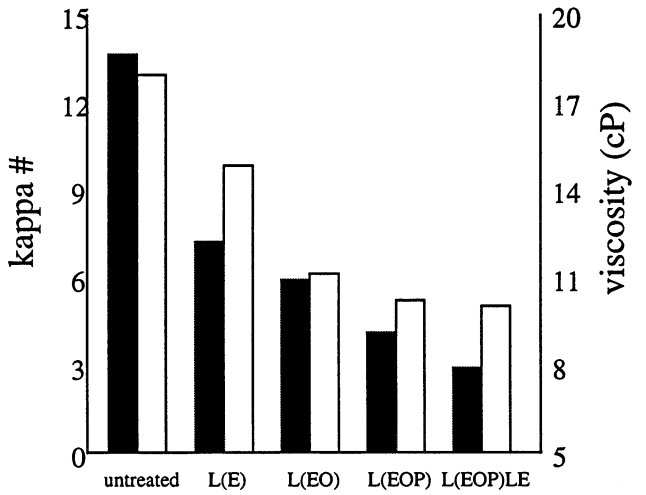
**Goal 2:** The bleachability of laccase/mediator delignified pulp was identified as an important issue this past fiscal year. This subtask was addressed by treating a softwood kraft pulp with laccase/N-hydroxybenzotriazole. As described last year, a typical laccase/N-hydroxybenzotriazole stage does not remove significant amounts of lignin. The majority of the lignin is released in a subsequent alkaline extraction stage. This two step process has been referred to as a LM-stage in the literature. Table 1 summarizes our experimental parameters for a LM-stage (Note: portions of this work contributed to J. Sealey Ph.D. studies). It should be noted that we have optimized the LM system for mediator and laccase charge but not for $O_2$ pressure or pH.

Table 1. Experimental conditions for a LM-stage.

| Stage | Conditions |
|---|---|
| Step 1. Laccase/mediator | Reaction time: 2-4 hr, pH:4.5, Temp.: 45°C, $O_2$ pressure: 10 barr<br>10% csc, 1.4 x 10-4 mols mediator/gr od pulp, approx. 60 x $10^3$ U of laccase |
| Step 2:Alkaline extract. | 10% csc, 1-2% charge N NaOH, 1 hr, 70°C. |

After the laccase/N-hydroxybenzotriazole treatment, the softwood kraft pulp was alkaline extracted. Along with our routine extraction procedure, (see Table 1) we investigated the effectiveness of an (EO) and (EOP) extraction for the laccase/mediator treated pulp. The results of these studies are shown in Figure 4. An EOP-stage was found to be most effective at removing lignin. This can be readily attributed to the presence of quinoid structures in the residual lignin after the laccase/mediator treatment.

Figure 4. Changes in kappa number and viscosity for a SW kraft pulp treated with laccase /mediator (L) and extracted using E, (EO), and (EOP).[1]

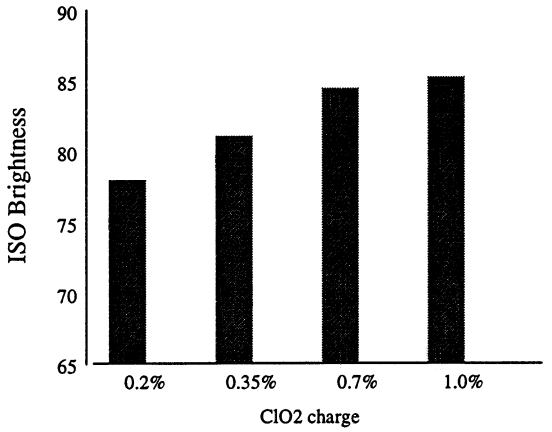



[1]L=laccase/Nhydroxybenzotriazole treatment; E:typical alkaline extraction stage; Note LE=(LM).

These results indicate that a routine laccase/mediator treatment followed by alkaline extraction can remove 48% of the lignin in the pulp. Reinforcing the alkaline extraction stage with oxygen increased delignification to 56% and the use of a typical (EOP) stage provided 65% delignification. The pulp yield after the L(EOP) treatment was found to be 97%.

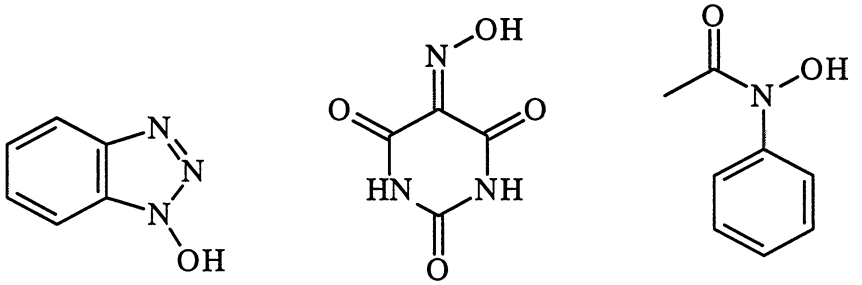
Interestingly, the use of a second LM stage on the L(EOP) pulp removed an additional 32% of the residual lignin. The L(EOP)(LE) bleached pulp was then bleached with a final D stage and these results are summarized in Figure 5.

Figure 5. ISO brightness values for SW kraft pulp bleached L(EOP)LED.[1]




[1]L=laccase/Nhydroxybenzotriazole treatment; E: typical alkaline extraction stage; Note LE=(LM).

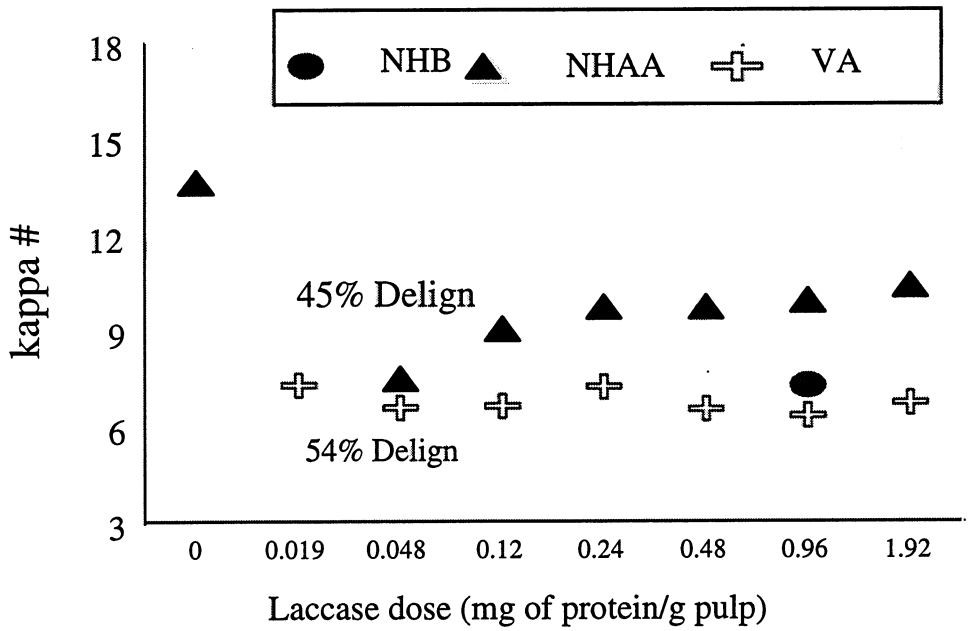
The final task in this sub-project for fiscal year 1997-98, was to determined the effect of a LM-stage on pulp strength properties. A LM (Note:N-hydroxybenzotraizole) delignified softwood kraft pulp was prepared for these studies but unanticipated new developments have delayed the physical testing studies. At the recent International Symposium on Wood and Pulping Chemistry, Amann presented a paper identifying two new mediators for laccase. (Lignozym® Process-Coming Closer to the Mill, F4-1-F4-5 (June 12, 1997)). The mediators, violuric acid (VA) and N-hydroxyacetanilide (NHAA) were proposed to be more cost effective for a LM-stage.




N-Hydroxybenzotriazole(NHB) Violuric Acid (VA) N-hydroxyacetanailide (NHAA)

Preliminary investigations by J. Sealey indicated that these two new mediators exhibited substantially improved delignification effects. As summarized in Figure 6, the use of violuric acid instead of N-hydroxybenzotriazole decreased the required enzyme charge by 97% without detrimentally impacting the extent of delignification.

Figure 6. Results from LM delignification of an oxygen delignified SW kraft pulp[1] using N-hydroxybenzotriazole, violuric acid, and N-hydroxyacetanilide as mediators.[2]




[1]starting kappa #:13.6; [2]NHB charge is optimal for this pulp. Note: VA provides slightly better delignification at 2.5% of the enzyme charge used for NHB.

This data, in essence, makes all further laccase work with N-hydroxybenzotriazole obsolete. It is interesting to note that Amann claims that NHAA is the best mediator for laccase and yet in our lab VA outperforms NHAA (see Fig 6). At this time we are uncertain if this is due to differences in laccase or other experimental factors.

With the support of the PAC committee, we anticipate studying this new mediator system and then re-addressing the strength performance issues.

**Goals 3:** The bleachability of chemically methylated pulps was examined this fiscal year. Previous studies (see PAC report FY 1996-97) had suggested that methylated pulps could be resistant to LM-delignification. This effect was further studied this fiscal year. A well washed softwood kraft pulp was methylated with an alkaline dimethylsulfate solution. Methoxy analysis of the pulp indicated that the starting pulp had a methoxy content of 1.2% (wt basis) and that after methylation it had increased to 2.5%.

Both the methylated pulp and the initial brownstock were then treated with a LM-stage (Mediator: N-hydroxybenzotriazole, Violuric acid) and changes in physical properties were measured. The results of these investigations are summarized in Table 2.

Table 2. Kappa number, klason lignin, and viscosity for softwood kraft pulp (methylated and non-methylated) before and after an LM-stage using N-hydroxybenzotriazole and violuric acid as mediators.

| Pulp | Kappa # | Klason Lignin | Viscosity/cP |
|---|---|---|---|
| **Softwood Kraft (SWK)** | 33.9 | 6.0 | 41.4 |
| **Methylated SW Kraft (MSWK)** | 24.1 | 6.1 | 33.5 |
| **LM-stage Mediator: HBT using SWK** | 27.1 | 5.9 | 33.5 |
| **LM-stage Mediator: VA using SWK** | 28.0 | 4.8 | 33.0 |
| **LM-stage Mediator: HBT using MSWK** | 19.6 | 5.4 | 28.6 |
| **LM-stage Mediator: VA using MSWK** | 21.9 | 4.7 | 28.6 |

Based on kappa measurements, the laccase/N-hydroxybenzotriazole system outperformed the laccase/violuric acid system for delignification of the methylated and underivatized softwood kraft pulps. (see Table 3)

Table 3. Percent delignification for methylated and underivatized softwood kraft pulps after an LM-stage using N-hydroxybenzotriazole and violuric acid as mediators.

| Pulp | LM-stage with HBT | LM-stage with VA |
|---|---|---|
| SW | 20 | 17 |
| MSW | 19 | 10 |

A comparison of the bleached pulps based on Klason lignin suggests that the laccase/ violuric acid mediator system is a better delignification system. Presumably, the Klason lignin determinations are a more accurate measurement of lignin and this result suggests that violuric acid may be preferred for delignification of kraft pulps.

Note: We typically achieve 30-45% delignification with a SW kraft pulp in the kappa range of 25-35. Unfortunately, this pulp sample did not respond in this manner. At this time we are uncertain if this is due to the pulp or perhaps the quality of the enzyme used for these experiments. This uncertainly limits the generality of the conclusions to be made in this section, nonetheless it appears that methylation of the pulp does not substantially impact the performance of a LM-stage. The same conclusion was also presented in the FY 1996-97 PAC spring report.

**Goal 4.** One possible commercial application of a LM-stage is the delignification of high kappa kraft pulps. This technology could be used to improve the overall yield of bleached kraft pulps by stopping a kraft cook in the bulk delignification stage where selectivity remains high. Currently, the only viable option for removing the significant amounts of lignin in high kappa pulps is the use of double stage oxygen delignification.

It is our hypothesis that a single or double LM-stage could provide a low capital alternative to double stage oxygen delignification providing improved yield and cost benefits. As a preliminary investigation into this field, we elected to study LM-delignification of a linerboard furnish. Employing un-optimized LM delignification conditions, a softwood kraft pulp with a kappa number of 92 was treated with laccase and mediator for 4 h. The experimental conditions and extent of delignification achieved is summarized in Table 4.

Table 4. Experimental LM conditions[1] and extent of delignification achieved with a 92.2 kappa softwood kraft pulp.

| Mediator Employed | Charge of Mediator | Final Kappa Number | % Delignification |
|---|---|---|---|
| N-hydroxybenzotriazole | 0.52% | 78.6 | 15% |
| N-hydroxybenzotriazole | 4.20% | 76.0 | 18% |
| Violuric Acid | 0.40% | 76.7 | 17% |
| control: no mediator no laccase | --- | 87.3 | 5% |

[1]all laccase mediator treatments employed 10 barr $O_2$, pH 4.5, 10% csc, 45°C, 4 hr and 1.75 x $10^5$ U of laccase/gr pulp. The proceeding alkaline extraction employed 2% NaOH, 10% csc for I hr at 70°C.

Although the LM-stage did not provide the typical 30 - 40% delignification we routinely observe for low kappa pulps, we believe these results are very encouraging. This data is the first experimental proof that a LM-stage can remove lignin from very high lignin content pulps. This study employed our best low kappa LM-delignification conditions which are undoubtedly ill-suited for high kappa pulps. It is anticipated that further research will be needed to optimize the LM-delignification of high-kappa kraft pulps. Nonetheless, the results in Table 4 justify further investigations into this field of laccase biobleaching.

## Experimental

Materials: All pulps employed in these studies were acquired from commercial operations throughout North America. All chemicals were commercially employed and used as received. Laccase, isolated from a *Polyporus* fungi, was kindly donated and used as received.

Laccase Assay: The activity of the laccase was measured by monitoring the rate of oxidation of syringaldazine. The change in $A_{530nm}$ of 0.001 per minute per mL of enzyme solution in a 100 mM potassium phosphate buffer (2.2 mL) and 0.216 mM syringaldazine in methanol (0.3 mL) was set to one Unit of activity. This test was performed at 23°C.

General Laccase/N-hydroxybenzotriazole Biobleaching Stage (LM stage). A 10% consistency pulp slurry (10 gr dry weight pulp) was added to a preheated pressure vessel maintained at 45°C. To this mixture, was added the N-hydroxybenzotriazole (0.2 gr, 0.0015 mols) and the resulting mixture was stirred for 3 min. The pH of the mixture was then adjusted to 4.5 with glacial acetic acid and the laccase containing solution (200 - 800 x $10^3$ U) was added. The pressure vessel was then sealed and the reactants were stirred for 4-24 h, at 45°C and 10 barr $O_2$ pressure. After treatment, the mixture was filtered, and the pulp fibers were washed with deionized water (2000 ml). The pulp fibers (10 g, 10% consistency) were then extracted with an aqueous 0.5 N NaOH solution for 1 h at 70°C. The pulp was then filtered, washed with water, air-dried, and physical properties were determined.

## Future Recommendations

The identification of new mediators that exhibit significantly improved delignification potential needs to be studied. The most important research issue is the need to determine why VA and NHAA significantly outperform NHB. To accomplish this goal we propose to:

- Determine the fate of VA and NHAA with softwood and hardwood kraft pulps;
- Examine the effects of mixtures of mediators to delignify kraft pulps with laccase;
- Begin optimizing the LM system for delignification of high kappa kraft pulps;
- Study physical properties of laccase/VA delignified kraft pulps.

## Research Benefits

The anticipated benefits of these studies include:

- New low-capital bleaching technology;
- Improved pulp yields;
- Reduced $ClO_2$ usage and chloride generation.

## Supporting Literature

Additional background information in the field of hexenuronic acids can be found in the following articles:

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# CHEMICAL FUNDAMENTALS OF BLEACHING - OXYGEN DELIGNIFICATION

## ANNUAL REPORT FOR F015 SUB-SECTION

Literature research has been initiated in the area of oxygen delignification in order to develop some fundamental understanding of past oxygen delignification research, to secure external funding for various exploratory projects, and to seek a postdoctoral fellow or technician who will devote his or her full-time to the project.

The enhanced use of molecular dioxygen as a commercial pulp bleaching agent is constrained by two prominent research issues: (1) **the lack of selectivity for delignification versus cellulose damage after 40-50% delignification of kraft pulp** and (2) **the delivery of oxygen to lignin**. In order to address research issue (1), fundamental research studies must be initiated that interrogate the factors which are responsible for controlling the selectivity of delignification. Research issue (2) is a more complex issue to tackle since the experimental factors controlling oxygen delignification include solubility in water and transfer to the lignin in the pulp. The thrust of the work will therefore be primarily directed toward analysis of the criteria which limit selectivity and also the examination of oxygen delivery. Clarification of the chemical factors which are involved in selectivity enhancement as well as the factors affecting transfer of oxygen to the lignin will allow the industry to develop strategies to enhance the use of oxygen which will a positive impact on pulp strength, yield, and brightness and aid in reducing the level of further bleaching chemicals and subsequent mill effluent.

Oxygen bleaching stages are being extensively used in pulp and paper mills throughout the world. In 1996 alone, almost 160,000 tons/day of the world's bleached kraft pulp production passed through an oxygen delignification stage. Oxygen stages are typically included in greenfield mill operations automatically, whereas most existing mills without an oxygen bleaching stage will retrofit the mill to include the stage. The most important factors for considering an oxygen delignification stage are environmental pressures, market demands, capital availability, and recovery boiler or chlorine dioxide capacity. Nonetheless, oxygen bleaching remains an effective and inexpensive method to maintain cost-effectiveness in the overall bleaching process by conserving the total amount of chlorine dioxide used. A very pressing issue that remains to be solved is increasing the total bleaching capacity without adversely affecting the quality of the polysaccharide component of pulp. The efficiency for selective delignification up to 40-50% of the residual lignin in mill applications has been realized, but further efforts to delignify result in losses in the polysaccharide component of the pulp.

The performance of oxygen bleaching can be optimized if a fundamental knowledge of the identity of reactive species resulting from oxidation were obtained, in addition to understanding the kinetics of reactivity of lignin under various oxygen conditions. Some of the most important reactive species are hydrogen and alkyl peroxides, hydroxyl radicals, superoxide, and molecular dioxygen. Implicating the mechanistic reactivity of the above oxidants in pulp has been quite challenging and little is known about their specific role and interplay in pulp bleaching. It is known, however, that hydroxyl radicals are extremely reactive species which preferentially attack lignin to carbohydrates by a ratio of 7/1. Yet, interestingly, the selectivity ratio becomes much less after approximately 50% total delignification of pulp. The nature of the pulp is undergoing chemical and structural changes during oxygen bleaching which certainly impact subsequent reactivity. It is known, for example, that pulp undergoes a very fast delig-

nification rate in the early phase of oxygen bleaching which subsequently begins to level off. Apparently, the reactivity of the pulp is modified very quickly in the early part of oxygen bleaching through structural changes resulting from oxygen bleaching. A fundamental understanding of the chemical changes occurring during oxygen bleaching is part of the thrust of the research in the present report. Some of the most important issues to tackle include the role of metallic ions in bleaching, the nature of the radicals generated during bleaching, and the fate of the lignin at the point where the carbohydrates begin to substantially degrade.

The second research issue involves elucidating the issue of mass transfer of oxygen through pulp and potentially improving the accessibility of oxygen to pulp. The mass transfer of oxygen may potentially have implications for the overall delignification efficiency since the kinetics of oxidation are biphasic, having a reaction order for the fast phase as well as one for the slow phase. From published reports, there is much conflict about the two reaction orders, which complicate the analysis of the transfer of oxygen; that is, in the fast phase does oxygen contribute significantly to the oxidation, but in the slow phase, does its activity diminish? What are the factors involved in the diminished activity of oxygen in the slow phase? Can oxygen bleaching be improved by reducing the consistency of the pulp? Some authors suggest that the consistency is critical to improving the bleaching efficiency. Yet, the understanding of the influence of consistency is far from complete, since the fiber aggregation of higher consistency pulps may itself serve to help bleaching by exposing more contact surface area (gas/solid transfer) allowing for direct oxidation.

Oxygen and its various derivative species which initiate oxidation reactions ($H_2O_2$, $O_3$, $HO^{\cdot}$, $O_2^{\cdot}$, $O^{\cdot-}$, $HO_2^{\cdot}$) have been implicated and/or exploited for the bleaching of kraft pulp. One highly reactive form of oxygen which has received little attention for oxygen bleaching of kraft pulp is *singlet oxygen* ($^1O_2$*). In the dark reactions of oxygen with pulp, researchers have speculated that singlet oxygen is generated from the decomposition of superoxide, but the concentration may be insufficient to have any appreciable reactivity. Photochemical generation of singlet oxygen is much more efficient and represents a tried and true method of generating singlet oxygen. Singlet oxygen is a strongly reactive, long-lived, and phosphorescent form of ground-state oxygen which has been implicated in molecular damage to living systems. In pulp, it has the capacity to degrade lignin as has been shown by Brunow in a 1978 study of the photoyellowing of lignin.

Many systems initiate the oxidation of lignin by thermally-induced electron transfer reactions. Electron transfer reactions are at the crux of oxygen delignification reactions and can be favored by reaction with an excited state species. For example, the electron transfer from phenolate residues to oxygen has a rate of about $10^{-4}$ $M^{-1}s^{-1}$; in the presence of a suitable excited state acceptor (for the research, $Ru(bpy)_3^{+2}$ will be used), the reaction can be enhanced by a factor of **10-1000 billion**. The kinetics and specificity of photoinduced electron transfer between lignin and an excited state acceptor will be exploited to improve oxygen delignification. The acceptor will be one that can easily migrate into the pulp and induce electron transfer.

# EXTERNAL-FUNDED PROJECT SUMMARY
# FY 1997-98

**Project Title**: Improved Selectivity in Ozone Bleaching

**Project Number**: 4168

**PAC**: Chemical Pulping and Bleaching

**Division**: Chemical and Biological Sciences

**Project Staff**
- **Faculty/Senior Staff**: Donald Dimmel
- **Staff**: Cathy Welder

**FY 97-98 Budget**: USDA New Research Initiative Program - $65,000

**Time Allocation**
- **Faculty/Senior Staff**: 15%
- **Support**: 70%

**Supporting Research**
- **Summer Intern Student**: John Werner
- **Internal**: F015, Chemical Fundaments of Bleaching

## RESEARCH LINE/ROADMAP:

Environmental Performance:
- Reduce emissions of entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule while maintaining global competitiveness.
- Reduce water usage in bleached kraft pulp production to 2500 gallons per ton.

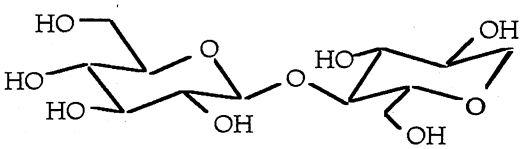
## PROJECT OBJECTIVE:

The use of ozone as a pulp bleaching agent is hampered by pulp quality issues; there appears to be ozone-induced cellulose chain cleavage reactions that effectively reduce the degree of polymerization (DP). Cellulose can potentially be depolymerized as a result of attack by ozone directly, by radicals derived from ozone decomposition in water, by radicals from ozone-phenol reactions, and/or by radicals from secondary decomposition of ozone-organic intermediates. The goal of this research project is to clarify the relative importance of these reaction pathways. Clarification of the reaction pathways will allow the industry to develop strategies to improve ozone selectivity which, in turn, has a positive impact on pulp strength, yield, and brightness and aids in reducing the level of bleach mill wastes.

## PROJECT BACKGROUND:

If carbohydrate degradation by ozone is a result of direct attack of ozone on C-H bonds, there is little that can be done about controlling ozone bleaching selectivity. However, if the selectivity problem is associated with certain types of byproduct radical reactions with carbohydrates, then possible protective measures could be sought. The extent of each of these reactions - direct ozone attack and byproduct radical attack - is a controversial subject. Hydroxyl radicals are believed to react rather indiscriminately with lignin and carbohydrates; lignin models react ~7 faster than carbohydrate models. Molecular ozone is reported to be ~1 million times more reactive with lignin-like compounds than with carbohydrate compounds. These large reactivity differences have led many scientists to conclude that radicals formed during ozone reactions are principally responsible for ozone's low selectivity with pulp. However, recent studies indicate that hydroxyl radicals only account for approximately one-third of the viscosity loss during the ozone degradation of cellulose, the rest is attributed to direct ozone reactions. It is clear that the role of radicals in ozone-induced carbohydrate degradation under various conditions remains to be resolved. This research is trying to provide information related to the role of different potential ozone pathways that lead to chain cleavage reactions and reduce cellulose DP (viscosity of pulp).

A much less structurally complex model system will allow us to follow various degradation reactions and develop an in-depth understanding of selectivity changes. Previous model studies have touched upon this fact, but have not been taken to the depth needed for a good understanding of the mechanisms involved. A good model is 1,5-anhydrocellobiitol (**1**), a disaccharide cellulose model; it is designed to resists "peeling" reactions and contains the identical β-(1-4) linkage present in cellulose. Ozone reactions with model **1** should provide information on reaction sites and product compositions; the methods used in the model case could then be applied to a more complex cellulose case. Of particular interest is the location and frequency of carbonyl and carboxyl groups.




**1**

A second substrate of high interest to us is amorphous cellulose; it should be an ideal cellulose substrate to study, since amorphous (disordered) regions are much more accessible to reagents than are crystalline (highly structured) regions. We believe that ozone selectivity can be effectively monitored by examining (1) molecular weight changes of amorphous cellulose and (2) the extent of degradation of lignin or a lignin model that is present during the cellulose ozonizations. The former provides information on polymer chain length, the latter pulp delignification efficiencies. The DP of amorphous cellulose will be followed by gel permeation chromatography (GPC).

## SUMMARY:

The reactions of ozone with 1,5-anhydrocellobiitol (**1**) under a variety of conditions, including cases where radical reactions should have been minimal, led to very complex reaction mixtures (>100 products). Glucose and 1,5-anhydrogluciitol, the two monomers composing the disaccharide model, were the major products, but each was found in less than 1-2% yield. Contrary to our expectations, it appears that **1** reacts with ozone non-selectively. This finding caused a significant change in the research direction.

We then concentrated on the ozone reactions of fluffed cotton linters, since the linters appear to have the same reactivity towards ozone as amorphous cellulose. Cellulose degradation by direct glycosidic bond cleavage was monitored by determining the drop in the DP of carbamylated, $NaBH_4$-reduced samples with gel permeation chromatography. The $NaBH_4$ reduction step was necessary, since the pyridine present in the carbamylation step induced carbohydrate chain cleavage reaction in non-reduced ozonated carbohydrate samples. We observed very little direct cellulose chain cleavage at ozone doses <10%; ozone doses used for bleaching are typically less than 1%. Low consistency ozonations caused less DP drop than high consistency ozonations. In the absence of lignin, it appears as if direct cellulose chain cleavage by ozone is minimal.

We are now examining different ozone doses and reaction times to decipher the importance of direct ozone attack versus ozone byproduct-induced degradation. Analysis of the ozone-treated samples before and after $NaBH_4$ reduction is another aspect of this study. In addition, we are examining the ozone reactions of cotton linters spiked with lignin to determine the affect of lignin-ozone reactions on cellulose degradation. An ideal substrate for studying ozone-pulp chemistry is a lignin carbohydrate complex (LCC). We have synthesized a model LCC, as a lead into preparing a cellulose LCC.

## GOALS FOR FY 97-98:

Our goals for the remaining three months of this fiscal year are:

- to complete a set of ozone reactions involving time and dose differences for fluffed cotton linters, with/without lignin and metals present, and with/without $NaBH_4$ reduction,
- to further evaluate the differences between ozone reactions of fluffed cotton linters and amorphous cellulose, with/without lignin and with/without $NaBH_4$ reduction, and
- to examine the ozone reactions of a fully acetylated 1,5-anhydrocellobiitol in organic solvents to gain possible insight into the reactivity of this type to disaccharide towards ozone.

# IMPROVED SELECTIVITY IN OZONE BLEACHING

## Annual Report for USDA-Funded Project 4168

**PROJECT OBJECTIVE**:

The use of ozone as a pulp bleaching agent is hampered by pulp quality issues; there appears to be ozone-induced cellulose chain cleavage reactions that effectively reduce the degree of polymerization (DP). Cellulose can potentially be depolymerized as a result of attack by ozone directly, by radicals derived from ozone decomposition in water, by radicals from ozone-phenol reactions, and/or by radicals from secondary decomposition of ozone-organic intermediates. The goal of this research project is to clarify the relative importance of these reaction pathways. Clarification of the reaction pathways will allow the industry to develop strategies to improve ozone selectivity which, in turn, has a positive impact on pulp strength, yield, and brightness and aids in reducing the level of bleach mill wastes.

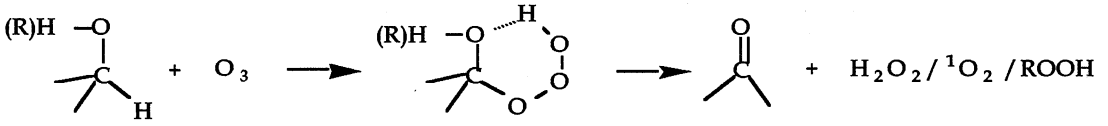
**PROJECT BACKGROUND**:

### *INTRODUCTION*

The strength deficiencies seen in pulps that have been bleached with ozone, and other oxygen-based bleaching systems, have their origin in greater amounts of cellulose chain cleavage reactions that effectively reduce the degree of polymerization (DP). There are several potential pathways of cellulose depolymerization; however, the relative importance of each of these pathways remains unclear. The loss in DP could be related to cellulose attack by ozone directly or by derived radicals. There are three potential sources of radicals in bleaching conditions: (1) decomposition of ozone, (2) decomposition of ozone-carbohydrate or ozone-lignin intermediates, or (3) production during ozone/phenol-OH reactions. The detailed chemistry of each pathway was presented, along with references, in last year's report; a brief summary is presented below.

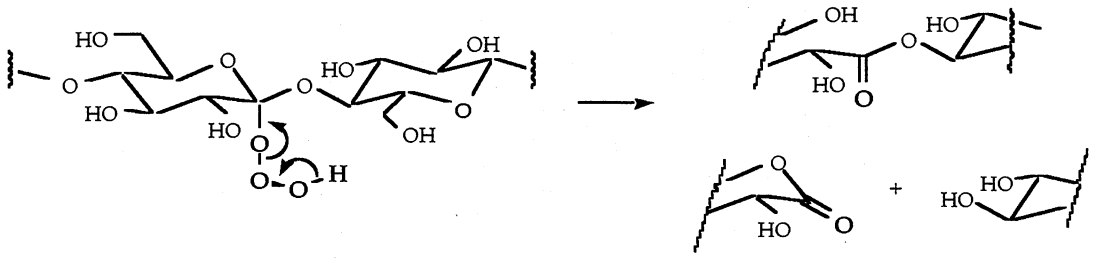
Direct Ozone Reactions With Carbohydrates

Carbon-hydrogen bonds are susceptible to ozone cleavage, including the activated anomeric carbon-hydrogen bonds in carbohydrates. Highly reactive hydrotrioxide intermediates are produced from the ozonation of acetals. When there is an oxygen atom adjacent to the insertion site, the hydrotrioxide may be stabilized by an intramolecular hydrogen bond (Equation 1).




(Eq. 1)

Once the hydrotrioxide intermediates are formed, they may decompose by ionic and/or radical pathways to provide carbonyl products. The major products from ozonation of β-methyl glycosides in aqueous solutions are gluconolactone and gluconic acid esters (Equation 2). Introduction of carbonyl and ester groups seriously affects the alkaline stability of carbohydrates. The low apparent viscosity of ozonated pulps, relative to strength properties, has also been attributed to carbonyl groups produced by ozone; peeling-type reactions occur during the alkaline viscosity assay. Reduction of carbonyl groups to alcohols retards degradation of $O_3$-treated pulps.



(Eq. 2)

Measurements of functional group concentrations in ozonized cellulose from pulp have shown that ozone only moderately increases carboxylic acid groups while carbonyl concentrations tend to fluctuate, but generally increase. Most of the carbonyl compounds are ketones. While these general trends are similar in most studies, it should be noted that the ratios of carboxylic acids to carbonyl compounds were different. These differences illustrate the difficulties in ascertaining the dominate reaction pathways of carbohydrate degradation.

Radicals in Ozone Reactions

Ozone decomposes in water to produce hydroxyl radicals (HO•), perhydroxyl radicals (HOO•), and superoxide radicals ($O_2^{\bullet -}$). The radical concentration increases at high pH and/or in the presence of metals. The two most important consequences of ozone decomposition are inefficient consumption of ozone and the production of the highly reactive radicals that are non-selective in their reactions with lignin and carbohydrates.

Radicals can also be produced by the homolytic cleavage of oxygen-oxygen bonds of hydrotrioxides; the cleavage leads to either reactive alkyperoxyl and hydroxyl radicals, or alkoxyl and hydroperoxyl radicals (Equation 3). Hydrotrioxides are generated by insertion of $O_3$ into carbohydrate and lignin C-H bonds (Equation 1).

$$\text{R-O-O-O-H} \rightarrow \text{R-O-O•} + \text{•O-H} \quad \text{or} \quad \text{R-O•} + \text{•O-O-H} \qquad \text{(Eq. 3)}$$

Ozone reactions with lignin can produce ozonides which decompose to carbonyl and α-hydroxy hydroperoxide fragments; these latter structures can produce reactive radicals by homolytic cleavage. In addition, investigators have proposed that ozone can react with phenolic groups (in lignin) to generate reactive HO• radicals.

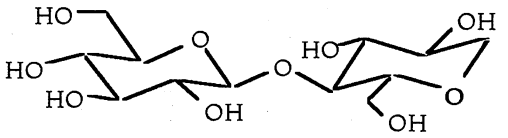
There is conflicting evidence as to the extent of radical involvement in carbohydrate-ozone reactions. Hydroxyl radicals are believed to react rather indiscriminately with lignin and carbohydrates; lignin models react ~7 faster than carbohydrate models. Molecular ozone is reported to be ~1 million times more reactive with lignin-like compounds than with carbohydrate compounds. These large reactivity differences have led many scientists to conclude that radicals formed during ozone reactions are principally responsible for ozone's low selectivity with pulp. However, recent studies indicate that hydroxyl radicals only account for approximately one-third of the viscosity loss during the ozone degradation of cellulose, the rest is attributed to direct ozone reactions. It is clear that the role of radicals in carbohydrate degradation during ozone bleaching under various conditions remains to be resolved.

## *EXPERIMENTAL PLAN*

The discussion below relates to our experimental plan at the start of the project. The Summary of Results section will indicate deviations that have occurred when obstacles were encountered.

### Selectivity Measurements

Selectivity measurements for pulp samples rely, to a first approximation, on determining the ratio of the change in kappa number to the change in viscosity during ozonation. While this seems simple, there are problems: (a) sample containing partially oxidized lignins will display a lower pulp kappa number than non-oxidized lignin and (b) the viscosity, which is related to carbohydrate DP and paper strength, frequently varies, in unexplainable ways, with the process. A much less structurally complex model system will allow us to follow various degradation reactions and develop an in-depth understanding of selectivity changes. Previous model studies have touched upon this fact, but have not been taken to the depth needed for a good understanding of the mechanisms involved. A good model is 1,5-anhydrocellobiitol (**1**); it is designed to resists "peeling" reactions and contains the identical β-(1-4) linkage present in cellulose.




**1**

Our intent is to develop methods that would provide information on reaction sites and product compositions for the reactions of ozone with model **1**, and then use the methods for the more complex cellulose case. Of particular interest is the location and frequency of carbonyl and carboxyl groups. Amorphous cellulose should be an ideal cellulose substrate to study, since amorphous (disordered) regions are much more accessible to reagents than are crystalline (highly structured) regions. The main reactions of wood carbohydrates are probably at amorphous regions; in part, the severe losses of hemicelluloses during pulping are related to the amorphous nature of this polymer.

We believe that the selectivity of bleaching reactions can be effectively monitored by examining the effects that bleaching chemicals have on amorphous cellulose and on mixtures of amorphous cellulose with lignin or lignin model compounds. Specifically, we plan to examine (1) viscosity and molecular weight changes of amorphous cellulose to determine differences in polymer chain length, and (2) the extent of degradation to a lignin or lignin model to determine pulp delignification efficiencies.

Mixtures of lignin models with carbohydrate models have been studied. However, problems with water solubility complicate the system. Most lignin monomer and dimer models are relatively insoluble in water under the acidic conditions employed during ozone bleaching. In such a case, the lignin models may associate and, thus, be less accessible (in comparison to actual lignin). Previous studies have tried to solve the solubility problem by using a mixture of water and organic solvent to obtain a homogeneous solution. The problem here is two-fold: (a) the model is soluble, while lignin is not during pulp ozonation, and (b) the organic solvent can scavenge radicals and greatly affect the reaction mechanism. We will attempt to adequately disperse any lignin model with the cellulose and avoid organic solvents. It may be possible to develop "intimacy" between the lignin model and cellulose by adding the lignin model to the cellulose solvent that is used to generate amorphous cellulose.

For ozone reactions of mixed systems composed of lignin or lignin model and cellulose, we will be looking for (a) molecular weight changes and carbonyl introduction in the cellulose and (b) the production of muconic acid structures and degradation products from the lignin (model). Unlike pulp, the model systems can use larger quantities of "lignin" to help facilitate the isolation and spectral investigations.

Selectivity Issues for Direct Ozone Attack

We will ozonize **1** and amorphous cellulose in the absence of metals and in the presence of radical scavengers; direct ozone reactions will be favored under such conditions. Reaction products will be identified and quantified, together with changes in polymer DP. To determine the role of carbohydrate-derived radicals on carbohydrate degradation, we will follow the course of the reaction with time. Changing product composition over time indicates a change in reaction mechanism. One explanation for a changing reaction mechanism would be that the initial products are a result of direct attack by ozone, while the slower developing products are due to by-products, such as ozone, carbohydrate, or lignin radical species.

Selectivity Issues for Radicals Derived from Ozone

To determine the role of radicals derived from ozone decomposition, we will expose 1,5-anhydrocellobiitol and amorphous cellulose (with and without lignin models present) to hydroxyl radicals. The latter will be generated from hydrogen peroxide and Fenton's reagent. The extent of degradation will be measured, and the products of model studies will be identified and quantified. It is expected that hydroxyl radicals will be much less discriminating in their reactions and, thus, provide

a different set of products than that obtained from direct ozone reactions. We anticipate that HO• will react to give carbonyl incorporation at nearly all -CHOH sites, while ozone will prefer reaction at C1. As appropriate, other radical species may also be investigated.

Selectivity Issues for Radicals Derived from Lignin

To determine the role of lignin-derived radicals on carbohydrate degradation, we plan to ozonize 1,5-anhydrocellobiitol and amorphous cellulose in the presence of lignin models and isolated lignin. The extent of lignin reaction with ozone will be compared to the degree to which 1,5-anhydrocellobiitol and amorphous cellulose are degraded. The DP of amorphous cellulose will be followed by viscosity and gel permeation chromatography (GPC). Reaction products will be identified, quantified, and compared to those obtained without lignin. If we find, for example, that the carbonyl distribution with amorphous cellulose is the same as that observed when amorphous cellulose is allowed to react with hydroxyl radicals, we can infer that hydroxyl radicals are being produced from ozone-lignin reactions. We will examine different lignin/cellulose ratios and reaction conditions, and the influence of lignin structure (phenolic, non-phenolic, etc.).

General Selectivity Issues

Bleaching selectivity depends on oxidant type and concentration, pulp consistency, pH, time, temperature, filtrate carry-over, mixing, solvent composition, and the presence of metals and additives. A thorough study of selectivity needs to consider all these factors. However, we will limit our study to those variables that are expected to be the most critical, such as the influence of metal ions. The best way to study metal effects is to add specific metals to the reaction medium.

## SUMMARY OF RESULTS:

Ozone Reactions with Cellulose Models

Last year's annual review presented our initial findings on the ozonations of the cellulose model 1,5-dianhydrocellobiitol. Carbon-13 nuclear magnetic resonance (NMR) spectroscopy indicated little if any reaction between 1,5-anhydrocellobiitol and ozone. Due to the low detection limits of NMR, we changed our method of analysis to gas chromatography (GC).

Acetylation of the products of the ozonation of 1,5-anhydrocellobiitol with acetic anhydride resulted in volatile products that were analyzed by GC. To our surprise, we detected more than 100 products by this sensitive method of analysis. We expected glucose and 1,5-dianhydroglucitol (the two monomers composing the disaccharide model) to be formed in high yield; however, they were found in less than 1-2% yield. Both were predominate products, in that the other products were formed in trace quantities. We have concluded that 1,5-anhydrocellobiitol reacts with ozone in an apparently non-selective fashion producing a multitude of products - each in a very low yield.

Several solvent systems were explored in order to find a more selective system. Reactions were carried out in an acetic acid/sodium acetate buffer, dilute acetic acid, 1% methanol, 1% methanol in the presence of dilute acetic acid, 75% methanol, and water. Neither the acidic conditions, nor the presence of a radical scavenger (methanol), improved the selectivity of the site of reaction of ozone with 1,5-dianhydrocellobiitol. Therefore, future studies with this model have been discontinued (indefinitely).

Ozone Reactions with Cotton Linters

Our original experimental plan proposed the study of the reaction of amorphous cellulose with ozone. We have discovered that it is difficult to derivatize amorphous cellulose, making it difficult to analyze the product of its reaction with ozone. We assumed, incorrectly, that amorphous cellulose would be more reactive both toward ozone and carbamylation reactions. Since fluffed cotton linters show similar reactivity toward ozone as the amorphous cellulose and are more easily prepared and analyzed, we now use fluffed cotton linters as our source of cellulose.

We have monitored cellulose degradation in $O_3$-cotton linters reactions by monitoring the drop in the DP. The latter was determined by first reducing the sample with $NaBH_4$, then derivatizing with phenyl isocyanate (PhNCO) in pyridine, and analyzing the carbamylated cellulose by GPC. The $NaBH_4$ treatment reduces carbonyl groups to alcohol groups. Protons on carbons that are alpha to carbonyl groups can be removed by base; the resulting carbanion can initiate a chain cleavage process. We have adopted a procedure reported by van Heiningen and co-workers to perform the $NaBH_4$ reductions.[1] The conditions involve using a 15% charge of $NaBH_4$ over 30 minutes at room temperature.

We have confirmed that the pyridine that is present in the carbamylation process is as destructive to ozonated cellulose as sodium hydroxide (E-stage), if the cellulose is not first reduced with $NaBH_4$. An ozonation was carried out with 1% consistency fluffed cotton linters, with a 10% ozone dose at pH 2.8 (pH adjusted with acetic acid). The ozonated cellulose was separated into three batches for different work up procedures, as indicated in Table 1. In each case, the sample was derivatized in duplicate with PhNCO. The data in the table show no significant difference in the weight average (Mw) DP and the number average (Mn) DP of ozone-treated, *non-reduced* cellulose samples that have come in contact with base prior to, or during, derivatization. In the one case where the sample was reduced with $NaBH_4$ before derivatization, the DP was much higher that the other two cases. The data indicate that carbonyl groups were present in the ozonated cellulose and that either NaOH or pyridine induced a DP drop in unreduced samples.

Ozonation experiments involving changes in consistency and ozone dose have been carried out in aqueous acetic acid at pH 2.80. The Mw DP and Mn DP data of the high consistency ozonations at varying ozone doses can be seen in Figure 1. Low ozone doses of approximately 1% and 10% resulted in little degradation of the cellulose polymer. A higher ozone dose of 100% resulted in a significant decrease in the DP of the cotton linters. It appears that at high consistency, ozone-induced degradation is not a problem for up to 10% ozone doses.

Table 1. DP differences as a result of work up of ozonated fluffed cotton linters.

| $O_3$-Pulp Treatment | Mn DP (duplicates) | Mn DP Ave. | Mw DP (duplicates) | Mw DP Ave. |
|---|---|---|---|---|
| pyridine/PhNCO | 2047, 1806 | 1926 | 4181, 3676 | 3928 |
| NaOH, then pyr./PhNCO | 1954, 2186 | 2070 | 3959, 4406 | 4182 |
| $NaBH_4$, then NaOH, then pyr./PhNCO | 2661, 2726 | 2694 | 4810, 4878 | 4844 |

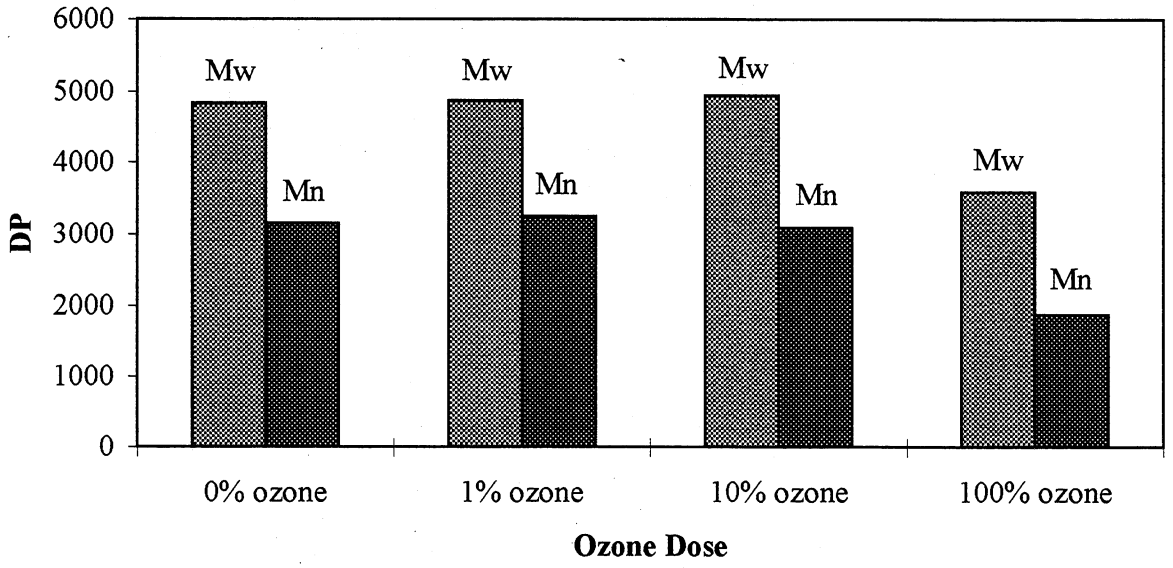



Figure 1. High Consistency Ozonations.

We have observed very little difference in cellulose degradation for reactions carried out at low consistency versus high consistency. Treatment of cotton linters at 1% consistency with ~10% ozone followed by $NaBH_4$ reduction and then carbamylation resulted in no loss in the Mw DP and only a 10% drop in the Mn DP. A small drop in Mn DP and virtually no drop in Mw DP implies that small chains and/or the ends of large polymer chains have been cleaved; either case results in only a small reduction in overall chain length.

At this point in our studies, we focused our attention on whether ozone itself degrades cellulose or one of its degradation products (such as hydroxide radicals) contributes to most of the observed DP drop. In order to carry out such a detailed study, we were forced to replace our ozone generator and change the design of the ozone flow. The older model ozone generator (that we had been using) forced us to use short application times for a low ozone dose and long application times for a high ozone dose. Since more than one variable was changed (ozone dose and application time), it was difficult to interpret the results of the experiments in terms of direct ozone attack versus ozone byproduct-induced degradations. Since ozone decomposes in aqueous solu-

tions, the difference in application time of ozone to a sample cannot be ignored. In order to overcome the problem, we switched to a newer ozone generator. The newer generator, and the resulting new ozone application design, allowed the time of ozone addition to be held constant with varying ozone dose.

We also solved other problems with this switch. The older ozone generator had become too unreliable. Ozone production rates dropped significantly over short time periods. Flow rates were also difficult to control. The instrument was designed for larger scale reactions. With small scale reactions (<0.5 g samples), a small fluctuation in ozone production results in a large relative error in ozone dose. The new ozone generator has a UV monitor in the line which displays the percent ozone production in the flow and allows for easy calculation of the applied ozone dose.

With the newer model ozone generator, high consistency ozonations were carried out with varying ozone doses at constant ozone addition times of 5 min. As can be seen in Figure 2, only a 10% Mw DP loss (25% Mn DP loss) was observed for the low dose (2.5% $O_3$) sample, while a larger ozone dose (29% $O_3$) resulted in a 34% drop in the Mw DP and a 50% Mn DP drop.

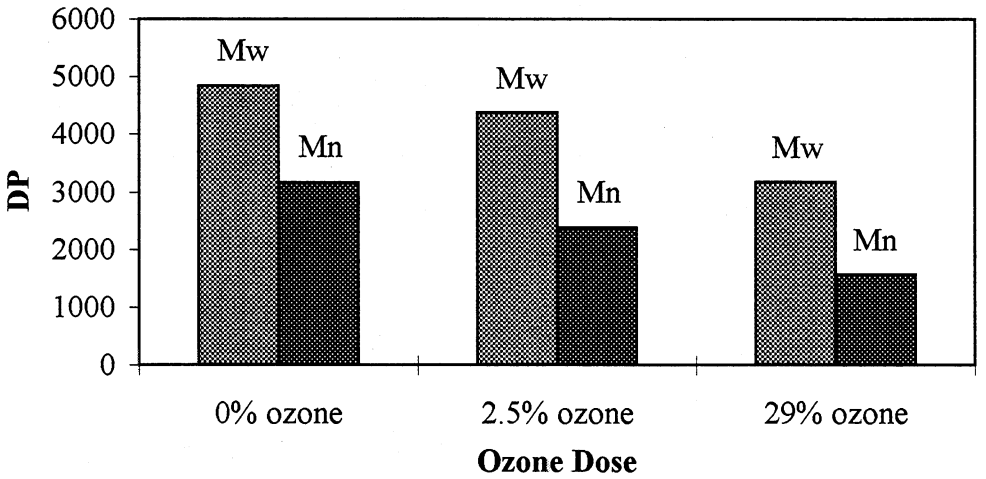



Figure 2. DP Drop as a Function of Ozone Dose.

It should be noted that a relatively large amount of ozone applied to a cotton linters sample (i.e., 2.5%) results in only a small amount of depolymerization. Ozone doses used for bleaching are typically less than 1%. *In the absence of lignin, it appears as if direct cellulose chain cleavage reactions by the action of ozone is minimal.*

Cellulose samples from low consistency ozonations retained their DP to a greater extent than did high consistency ozonations carried out under otherwise identical conditions. As shown in Figure 3, a low ozone dose of 2.6% had little effect on the DP of the cellulose. The higher ozone dose of 29% did result in more cellulose damage, as expected.

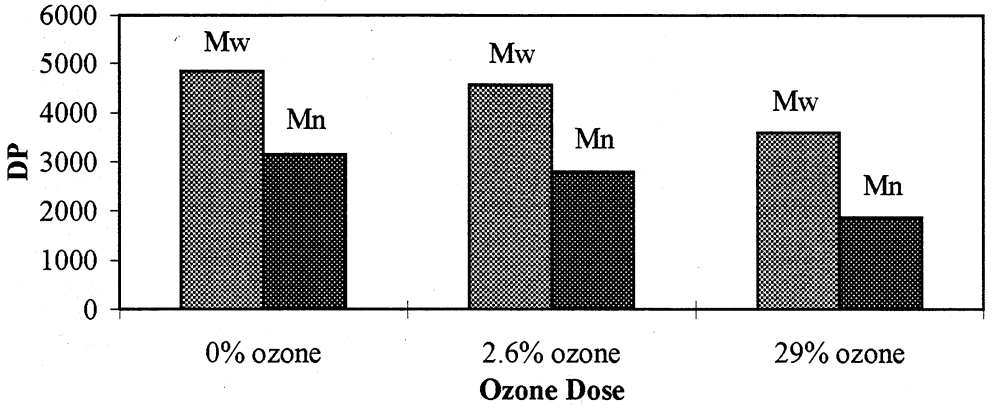



Figure 3. Low Consistency Ozonations.

In order to gain an understanding as to whether the observed degradation is due to direct ozone attack or attack by ozone decomposition products, we carried out reactions in which the ozone only came in contact with the cotton linters sample for 60 sec. (as opposed to 5 min., as presented above.) We suspect that shorter ozonation times will result in less ozone decomposition, which in turn, will result in less interference in the mechanism of the reaction by ozone byproducts. Degradation of cellulose during the shorter reaction times (60 s) appears to be similar to the degradation found during the longer reaction times (5 min). However, since two variables (ozone doze and reaction time) were changed in the last set of experiments, we will need to perform additional experiments before firm conclusions can be drawn.

Ozone Reactions with Cotton Linters Spiked with Lignin

A sample of cotton linters spiked with lignin was prepared by the addition of organosolv lignin in ethanol to fluffed linters. After evaporation of the ethanol, the linters were thoroughly washed with water. The filtrate was collected and concentrated to isolate the lignin in the wash. For comparison, Klaison lignin and acid-soluble lignin analyses were carried out on the spiked linters. The lignin content of the cotton linter sample was determined to be 1.7% which corresponds to a kappa number of 11.

We have just begun ozonations of the spiked cotton linters. The data of one study carried out at low consistency and another carried out at high consistency are shown in Figure 4. It is again apparent that degradation was less in the low consistency experiments. Notice, however, that less degradation was observed for spiked cotton linters than is typically observed for pulp. The explanation may lie in the fact that in a pulp sample the lignin is distributed evenly among the fibers, while in the spiked linters sample the lignin may only be attached weakly to the surface of the fibers. Ozone may be consumed by lignin-fiber surface reactions in the spiked linters sample in preference to penetration into regions that are principally cellulose. Experiments are needed to support this theory.

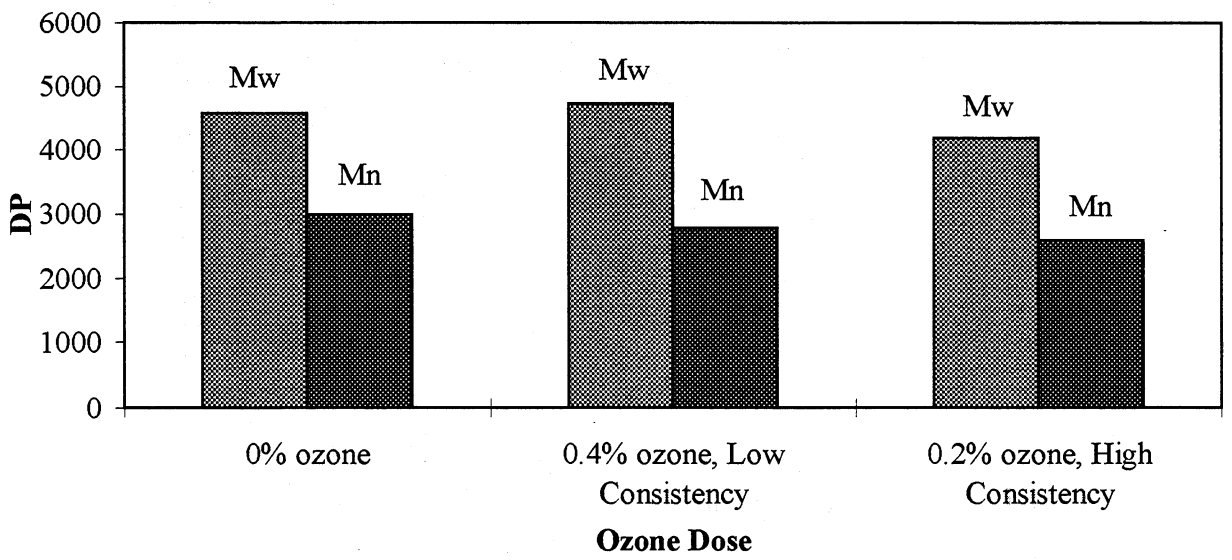


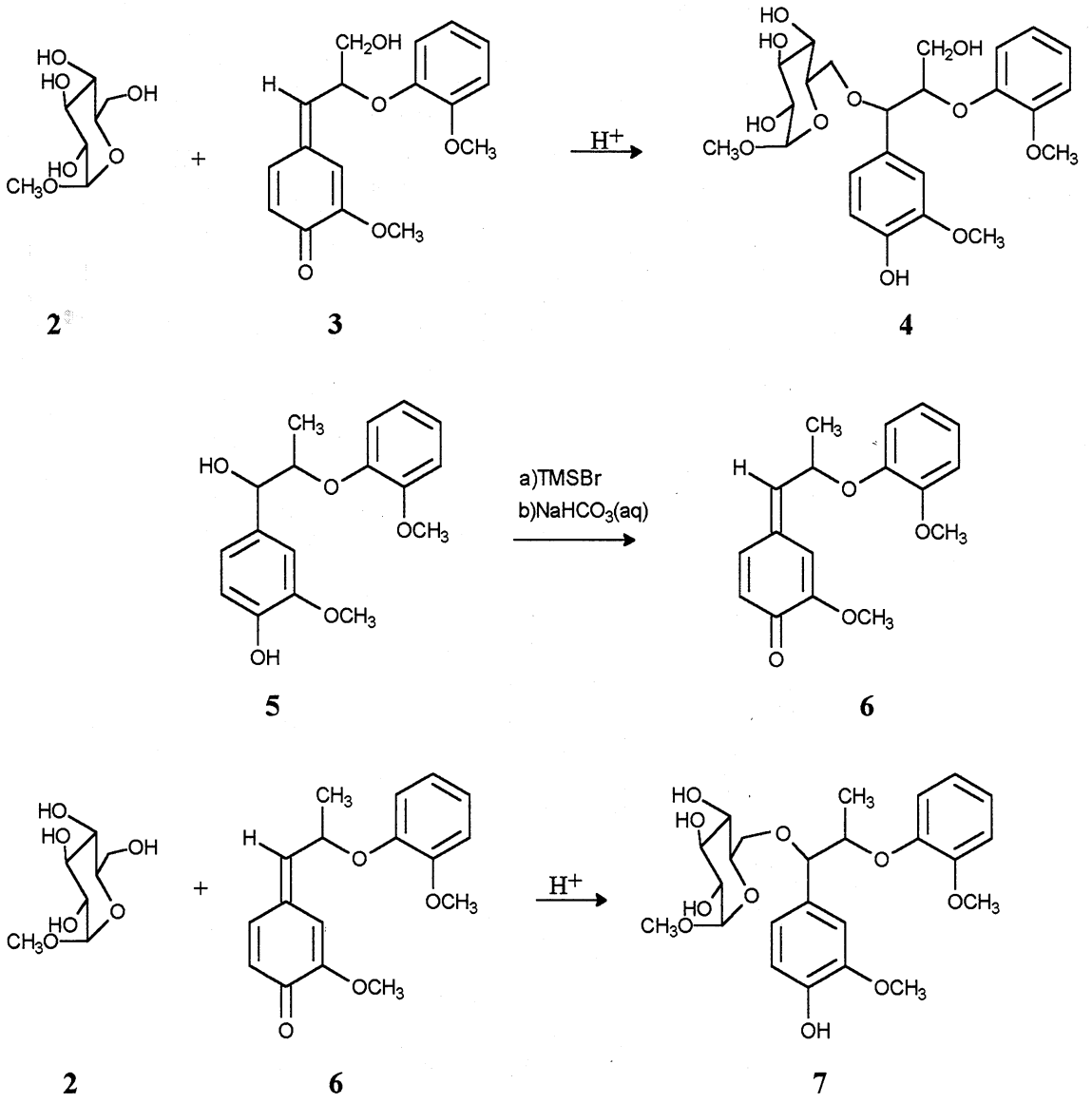

Figure 4. Ozonation of Spiked Cotton Linters.

Studies have been carried out to determine the statistical reproducibility of the GPC data. It has been determined that a less than 2% standard deviation is obtained for both the number and weight average DP. This reproducibility is superb for the GPC technique. Also, considerable time has been devoted to methods development associated with delivering proper ozone doses and with cellulose derivatization and analysis; however, we are now in a position to carry out the mechanistic studies at a much faster pace, even though the analysis of each sample is quite time consuming.

Synthesis of Lignin-Carbohydrate Complex Models

An ideal substrate for studying ozone-pulp chemistry is a lignin carbohydrate complex (LCC). Such structures probably account for a significant portion of the lignin present in unbleached pulp. We sought to synthesis a cellulose-type LCC - a novel model polymer. Before tackling this potentially difficult synthesis, we decided to first prepare a non-polymeric LCC. Brunow and Sipila[2] have reported the acid-catalyzed synthesis of LCC **4** from methyl-α-D-glucopyranoside (**2**) and quinone methide **3** in 30% yield. We have previous used a method of Ralph and Young[3] to synthesize quinone methide **6** from compound **5** in quantitative yield. Since we have compound **5** available in our lab, we attempted to prepared model LCC **7** from the quinone methide **6** using Brunow's procedure. The various synthetic steps are indicated below.

Several different reaction conditions were employed before a successful synthesis of LCC **7** was obtained. We confirmed the structure of LCC **7** by both $^{1}$H- and $^{13}$C-NMR. Unfortunately, we only obtained an 8% overall yield in the conversion of lignin model compound **5** to LCC **7**. Experiments have begun in the synthesis of a lignin model - amorphous cellulose type LCC. Upon synthesis of the amorphous cellulose LCC, we will subject it to ozone bleaching.

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# CLOSED MILL OPERATION

Status Report for Project F017

Alan Rudie
Narendra Patel
Alan Ball

March 24-25, 1998

**DUES-FUNDED PROJECT SUMMARY**
**FY 1997-98**

| | |
|---|---|
| **Project Title:** | Closed Mill Operation |
| **Project Code:** | CLDMIL |
| **Project Number:** | F017 |
| **PAC:** | Chemical Pulping and Bleaching |
| **Division:** | Chemical and Biological Sciences |
| **Project Staff** | |
| **Faculty/Senior Staff:** | Alan Rudie, Earl Malcolm, Peter Pfromm, Junyong Zhu, Jeff Empie, Jim Frederick, Jian Li |
| **Staff:** | Clark Woitkovich, Chuck Courchene, Narendra Patel, Alan Ball |
| **FY 97-98 Budget:** | |
| **Allocated as Matching Funds:** | **$200,000** |
| **Time Allocation** | |
| **Faculty/Senior Staff:** | 10% |
| **Support:** | 50% |
| **Supporting Research** | |
| **M.S. Students:** | Ana Pucket (M.S. 1999) |
| **Ph.D. Students:** | Giselle Ow Yang |
| **External:** | Georgia TIP$^3$ No PP98-MP4 (4188), $57,500 annually, Rudie<br>Georgia TIP$^3$ No PP98-MP1 (4153), $112,385 (FY98), Woitkovich<br>DOE (Oregon State University, Frederick) |

**RESEARCH LINE/ROADMAP**:
4: Reduce Water Usage in Bleached Kraft Pulp Production to 2500 gallons per ton.

**PROJECT OBJECTIVE**: Develop technology useful in moving toward low effluent operation. Close coordination required with Project F013, F015, and F019.

**SUB-OBJECTIVE**: Produce "equilibrium" constants suitable for predicting metals partitioning between wood fibers and process filtrates.

**PROJECT BACKGROUND**:
Metals management in the paper industry has been around for a long time, principally related to control of transition metals in peroxide bleaching of high-yield pulps. The recent interest in alternative bleaching chemicals and in eliminating the bleach plant wastewater stream has added a new dimension to the metals management problem. The problem with metals buildup and inorganic scale formation in low effluent and closed mills has created a need for a much better understanding of metal binding in wood pulp.

**SUMMARY OF RESULTS**:
The ion exchange selectivity coefficient has been evaluated for determining the partition of metals between solution and pulp fibers. Under the controlled conditions of the experiments, the method accurately models the ion exchange isotherms for all binary

pairs evaluated and is accurate up to approximately 0.05 molar concentrations. Room temperature selectivity coefficients have been determined for the calcium/hydrogen, calcium/sodium, calcium/magnesium, calcium/manganese, calcium/barium, magnesium/barium, and the magnesium/manganese cases. Additional experiments with a linerboard grade softwood gave nearly identical selectivity coefficients to the results obtained with the bleachable grade softwood pulp. Recent experiments with a linerboard grade hardwood give slightly different selectivity coefficients than obtained in softwoods.

The calcium exchange experiments with protons (acid) and sodium provide evidence for different types of ion exchange sites in pulp. Because this is most apparent in the ion exchange processes comparing monovalent cations with divalent cations, it is evidence that the close proximity of some acid groups resulting in a chelating effect with the multivalent metals.

The selectivity coefficient is an accurate model for ion exchange at solution concentrations below the acid group concentration of the swollen fiber. Using the deviation from theory at high ionic strengths, it can be shown that about 0.3 grams of water are absorbed to the fiber and unavailable for solvating anions and cations.

**GOALS FOR FY 97-98**:

1. Development of validated NPE partitioning models:
   Simulation capabilities based on free energy minimization will be developed and validated. Work will be partially funded by DOE and done in conjunction with faculty at Oregon State University.

2. Evaluation of metal binding to wood pulp will include:

   - Complete competitive binding experiments between H+, $Ca^{++}$, $Na^{+}$, $Mg^{++}$, and $Mn^{++}$.
   - Complete the analysis of Selectivity Coefficients for H+, $Ca^{++}$, $Na^{+}$, $Mg^{++}$, and $Mn^{++}$.
   - Complete the analysis of the existing EXAFS spectra of tightly bound iron, and begin the preparation and analysis of suitable chemical models of the binding site.

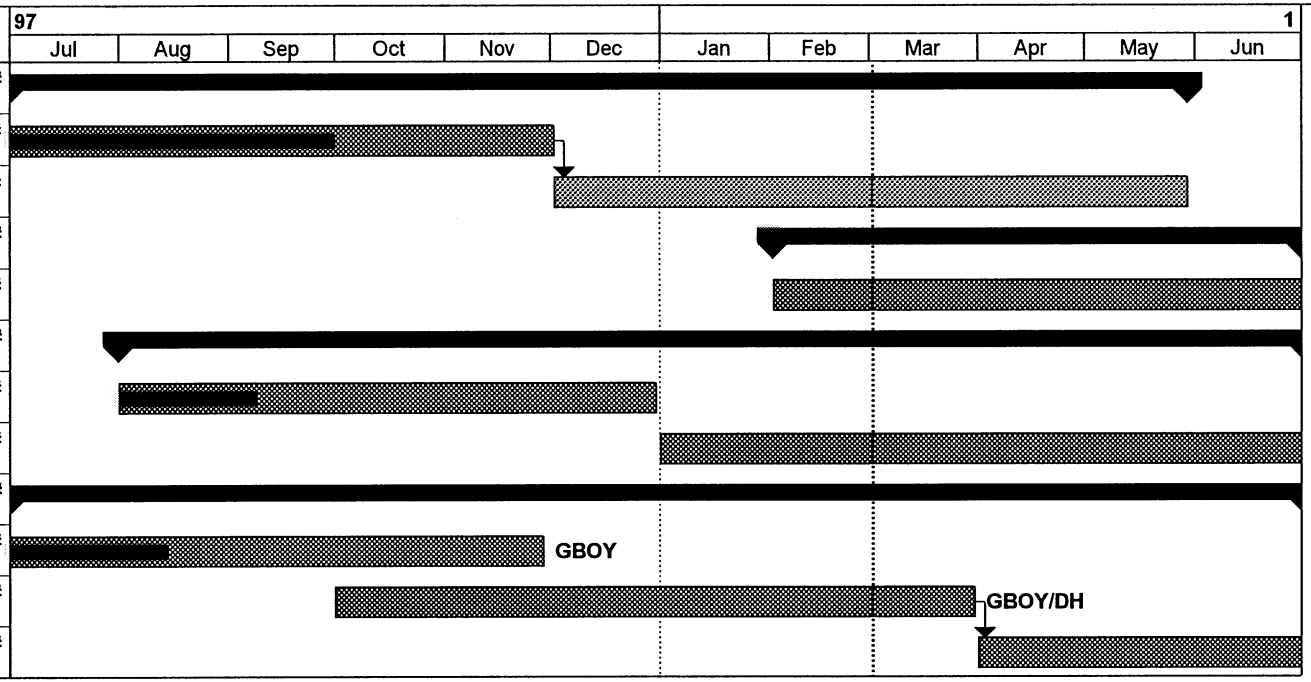
**DELIVERABLES**:

This project will produce a consistent set of equilibrium/free energy constants capable of predicting metals distribution between wood pulp and filtrates and will define the conditions under which the constants are valid.

**SCHEDULE:** The attached Gantt chart is for F017 and associated projects. Tasks 2 and 3 are Dues Funded Project F017. Task 5 is being carried out under Georgia $TIP^3$ PP98-MP1 (Clark Woitkovich) , tasks 7 and 8 are DOE (Jim Frederick, OSU) and tasks 10,11and 12 are a Ph.D. project, and Georgia $TIP^3$ PP98-MP4.

# Closed Mill Project (F017, DOE and GC)

| ID | Task Name | Start |
|---|---|---|
| 1 | **Selectivity Coefficients unbleached** | ######## |
| 2 | room temperature | ######## |
| 3 | elevated temperature | ######## |
| 4 | **Selectivity Coefficients, bleached** | ######## |
| 5 | room temperature | ######## |
| 6 | **Black Liquor (Agenda 2020)** | ######## |
| 7 | Sodium (Hydrogen and Calcium) | ######## |
| 8 | elevated Temperature | ######## |
| 9 | **Fe/EXAFS** | ######## |
| 10 | Fe Guaiacol Model | ######## |
| 11 | Ca and Mn EXAFS | ######## |
| 12 | Mn chemical Model | ######## |




Project:
Date: Mon 3/2/98

Task
Progress
Milestone
Summary
Rolled Up Task
Rolled Up Milestone
Rolled Up Progress

# ANNUAL REPORT; PROJECT F017
## Closed Mill - Metals Equilibria

By: Alan Rudie

## ABSTRACT

The ion exchange selectivity coefficient has been evaluated for determining the partition of metals between solution and pulp fibers. Under the controlled conditions of the experiments, the method accurately models the ion exchange isotherms for all binary pairs evaluated and is accurate up to approximately 0.05 molar concentrations. Room temperature selectivity coefficients have been determined for the calcium/hydrogen, calcium/sodium, calcium/magnesium, calcium/manganese, calcium/barium, magnesium/barium, and the magnesium/manganese cases. Additional experiments with a linerboard grade softwood gave nearly identical selectivity coefficients to the results obtained with the bleachable grade softwood pulp. Experiments with a linerboard grade hardwood give slightly different selectivity coefficients than obtained in softwoods.

The calcium exchange experiments with protons (acid) and sodium provide evidence for different types of ion exchange sites in pulp. Because this is most apparent in the ion exchange processes comparing monovalent cations with divalent cations, it is evidence that the close proximity of some acid groups resulting in a chelating effect with the multivalent metals.

The selectivity coefficient is an accurate model for ion exchange at solution concentrations below the acid group concentration of the swollen fiber. Using the deviation from theory at high ionic strengths, it can be shown that about 0.3 grams of water are absorbed to the fiber and unavailable for solvating anions and cations.

## INTRODUCTION

Metals management in the paper industry has been around for a long time, principally related to control of transition metals in peroxide bleaching of high-yield pulps.[1] The recent interest in alternative bleaching chemicals and in eliminating the bleach plant wastewater stream has added a new dimension to the metals management problem. The problem with metals buildup and inorganic scale formation in low effluent and closed mills[2,3] has created a need for a much better understanding of metal binding in wood pulp.

There are several approaches to metals control currently employed in closed or low effluent mills. The low pH in an initial Chlorine Dioxide bleach stage is effective for stripping metals from the pulp. In Totally Chlorine Free bleaching (TCF), acid leaching and DTPA chelation have been evaluated under a variety of conditions. These methods successfully remove more than 90% of the manganese, calcium, and magnesium, but only about 50% of iron.[4] Strategies employed by low effluent mills include treating this filtrate stream to remove metals and reuse of the filtrate in the bleach plant or in brown stock washing,[5] or a controlled discharge of sufficient filtrate to control the metals buildup. Under some conditions, the metals remaining in the pulp after treatment can still affect bleaching efficiency and bleach plant operation.[6] Increasing the chelant dose, or treatment temperature, and extending the treatment time can improve metals removal efficiency to an extent, but on manganese, DTPA doses

above 0.2% on pulp, treatment temperatures greater than 75°C, and treatment times beyond 30 minutes show little incremental gain.[7]

Key technologies required to make the closed mill effort successful are improved and cost-effective metals removal from wood pulp, cost-effective metals removal from filtrates, and improved material and energy balances to help in engineering and controlling the low effluent mill. Accurate models of metal binding are needed so that mills and engineering firms can estimate the distribution of metals in the process and develop solutions that prevent scale formation and bleach chemical decomposition. Initial efforts to understand metal binding in pulp used solution equilibrium expressions to model the binding behavior.[7]

A solution equilibrium calculation for metal binding to pulp requires solving the acid dissociation constant for the acid functional groups in pulp (generally assumed to be carboxylic acids) and the formation constant equation for the metal with the acid binding site.

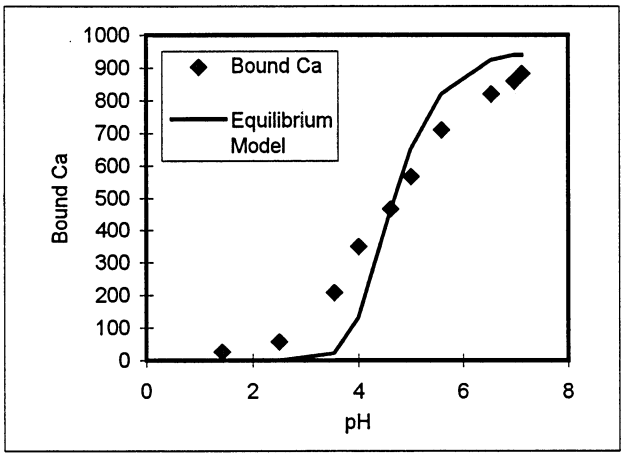



Figure 1. Solution equilibrium model for calcium binding to wood pulp.

The chemical theory for acid equilibria in homogeneous solutions generally abides by the following chemical and mathematical equations:

$$HA \rightarrow H^+ + A^-$$

and

$$K_a = [H^+][A^-]/[HA]$$

where $A^-$ is the conjugate base of acid HA, and $K_a$ is the appropriate acid dissociation constant.

The metal binding follows the chemical formation equation,

$$xA^- + M^{x+} \rightarrow MA_x$$

and

$$K_f = [MA_x]/([M^{x+}][A^-]^X)$$

where $K_f$ is the formation constant for the counterion with the dissociated fiber bound anion. Figure 1 shows an acid base Calcium formation equilibrium calculation using this solution equilibrium approach. Clearly this method fails to match the data near a pH of 3 and around a pH of 5.

Laine et al. claim this acid/base behavior of pulp is evidence for two different carboxylic acid functional groups, one at a pKa of 3.3-3.5 and the second with a pKa above 5.[8] The two-acid model predicts a slight deflection from the experimental data at a pH around 4, so they also invoke an electrical double layer/capacitance effect to completely explain their results. The Laine approach increases the complexity and has yet to provide a credible source for the second ion exchange site with a pKa above 5.

Metal binding to wood pulp is a complex process that involves aspects of surface charge (electrical double layer), Donnan Equilibrium (concentration differences between the solution and fiber), and metal complex formation. Under most conditions, wood fibers carry a negative charge, generally attributed to the presence of acid groups in the fiber.[9,10] The existence of this negative charge is the impetus for the myriad of wet-end chemicals and surface-active agents used to improve retention and formations on the paper machine. The presence of this charge also affects metal binding, because the metal cations are attracted to the negatively charged fibers, and the higher the charge on the cation, the greater the surface attraction. The acid groups in pulp have three major sources. The Xylan (arabino-xylan) portion of the wood hemicellulose contains side chain 4-O-methyl-D-glucuronic acids,[11] which have a $C_6$ carboxylic acid functional group. End groups on cellulose and hemicellulose contain carboxylic acid functional groups, and residual lignin contains a number of carboxylic acid functional groups. Typically, carboxylic acids have a pKa between 4 and 5, but this can vary significantly depending on the presence of other electron donating or withdrawing groups, and proximity to other acid functional groups. The pKa reported for glucuronic acid is considerably lower, at 3.3.[8] At normal mill pH's, some or all of the acid groups are hydrolyzed resulting in a negatively charged fiber. However, the principle of electroneutrality cannot be violated; the negatively charged acid sites must have associated with them an equal number of positive charges, either protons or other cations, and the net surface charge is but a small portion of the total acid content of the fiber.[12] (The principle of electroneutrality does not prevent the formation of a surface charge; it simply states that the number of anionic sites and associated cations is equal within analytical limits.) Therefore, the fiber will collect metal cations whether there is a significant binding potential between the cation and the acid group or not. Furthermore, there does not have to be a direct bond between cations and the specific charge sites. If other functional groups within the fiber matrix provide a more suitable ligand, the metal will bind to it preferentially. Technically, like the various cations, the acid groups serve only to maintain electroneutrality..

In dealing with a heterogeneous system such as a wood pulp slurry, several potential problems become apparent. Principal among these is that the effective concentration of bound acid [HA] and conjugate base [$A^-$] cannot be based on the solution volume because these functional groups are not free to disperse throughout the solution. Secondly, as stated above, the chemical entity $A^-$ does not exit on an analytical scale, it is always associated with an appropriate cation to balance the charge. The difficulty this presents is that there will always be a measurable equilibrium between a metal, or protons and the fiber, but that equilibrium can be driven by the electrostatic effects, and may not represent the ability of the metal to compete against other metals for sites on the fiber.

The Donnan theory was developed to explain ion distribution across a semipermeable membrane where one or more ions were excluded because of size or membrane selectivity.[13] The theory can consider effects of neutral materials, dissolved ions, and salts. With salts, where complete dissociation cannot be assumed, the theory must include the use of appropriate solution equilibrium constants to correctly calculate solution concentrations and ionic strength. In the Donnan theory, one or more ionic constituents are trapped to (or in) a portion of the system. This can be caused by a semipermeable membrane, or ionic groups confined to a swollen polymer such as an ion exchange resin. The natural tendency is for each constituent to diffuse uniformly throughout the solution. Where this is not impeded, it produces a balance of concentrations, ionic strengths, and charge. When one ion is restrained, complete and uniform distribution of the remaining ions would result in a charge buildup across the barrier (or inside the ion exchange resin), with the site of the trapped ion attaining the charge

of that ion, and the free solution the opposite charge. This charge difference is the Donnan Potential. So in a cation exchange resin (like the wood fibers) where the trapped functional group is an anion, the resin attains a net negative charge, and the solution a net positive charge. This negative charge repels the free anions in the surrounding solution, and attracts the free cations in the surrounding solution. The net result is that the resin becomes enriched in free cations, and depleted of free anions. Compared to a simple solution case, the principle of uniform distribution of all constituents has been violated to maintain the charge neutrality (or near charge neutrality) of the resin.

A second feature of the ion exchange resin also violates the principle of uniform distribution of all ions. The resin has a fixed ionic strength, dictated by the distribution or concentration of ionic groups in the resin. Under most conditions, this ionic strength differs from that of the surrounding solution, and is often considerably higher. This typically results in diffusion of water into the resin to reduce the ionic concentration and bring it into balance with the surrounding solution.[14] In a typical kraft pulp, the acid content is between 50 and 100 meq/kg; on a molar basis, 0.05 to 0.1 Molar. Under typical conditions, the fiber absorbs a considerable amount of water, 1 to 2 grams of water per gram of fiber. [15] If the Water Retention Value is considered to be the amount of water absorbed by the fiber to dilute the ion concentration, this reduces the acid group concentration to 0.02 to 0.04 Molar. At high solution pH, the acid group content, concentration, and ion exchange behavior must also account for the phenolic contribution from lignin.

When the ionic strength of the solution equals or exceeds the ionic content of the fiber and "bound" water, the behavior of the resin changes.[16] At this point, there is no longer a driving force to absorb water, and the fibers begin to shrink or de-swell.[15] Also at this point, the driving force that repels mobile anions is reduced, the Donnan Potential disappears, and the fiber begins to absorb anions and cations in approximately equal amounts.[15]

The attraction of the resin for cations and repulsion of anions can be calculated from the Donnan Potential, which is dependent on the charge of the cations (or anions), ion exchange capacity of the resin, solution conductivity, solution concentrations, and the degree of swelling of the ion exchange resin. Multivalent counterions are attracted more strongly, and absorbed selectively over monovalent counterions. Concurrently, multivalent co-ions (ions with the same charge as the functional group of the matrix) are repelled more strongly than monovalent co-ions.

The strength of the Donnan theory is that it handles a wide range of ionic strengths, and can largely calculate ion exchange behavior from first principles, without the need for determining specific ion behaviors. The disadvantage include:

1. The calculations are based on concentrations of free ions. Where bonding exists between the functional group of the resin and cations in solution, the Donnan Potential and Donnan selectivity break down. In the original Donnan Equilibrium theory for distribution across a semipermeable membrane, this is handled with the appropriate complex formation equilibria.
2. The distribution constant $\lambda$ is experimentally determined and is anything but constant. At low ionic strengths, it can vary from near 1 to $10^5$. At higher ionic strengths, it may only vary by a factor of 3.[15]
3. As concluded by Rasanen and Stenius, protons are not distributed according to the Donnan Equilibrium.[17]

Recent articles by Towers and Scallan[18] and Rasanen and Stenius[17] support the Donnan theory in that the results appear to explain the differences in behavior of monovalent, divalent, and trivalent metals, but these results still have considerable error in the pH regions from 3.0 to 3.5 and around pH 5.

**Selectivity Coefficients**

A second approach to explain ion exchange is quite similar to standard solution equilibrium theory. For acids, the acid dissociation is defined as

$HA \rightarrow H^+ + A^-$

and the equilibrium expression as written as

$K_a = [H^+][A^-]/[HA]$

where $A^-$ is the conjugate base of acid HA, and $K_a$ is the appropriate acid dissociation constant.

The metal binding follows the chemical formation equation,

$xA^- + M^{x+} \rightarrow MA_x$

and the equilibrium equation is written as

$K_f = [MA_x]/([M^{x+}][A^-]^X)$

**(Note, acid dissociation is inverted relative to the expression for formation equilibria.)**

The product of the acid dissociation and formation equations (replacing $A^-$ with $R^-$ to represent the bound anion) is defined as the selectivity coefficient, $K_H^M$.[19]

$$K_a K_f = K_H^M = \frac{[MR_x][H^+]^x[R^-]^x}{[HR]^x[M^{x+}][R^-]^x}$$

where the coefficient x represents the number of ion exchange sites occupied or neutralized by the metal. Usually, this will balance the respective charges, but in the case of trivalent metals, and in some cases with divalent metals, the cation can enter the fiber with associated anions and under these conditions, may account for fewer sites.

Several features of this equilibrium expression make it attractive. The term $R^-$ drops out of the expression. Because $R^-$ (anionic sites that do not contain a directly bound or solvated but still fiber bound cation) is small (principal of charge neutrality), it cannot be easily measured. Having it drop out of the equation is quite convenient. Secondly, for systems where both cations have the same stoichiometry, the concentration basis for MR and HR becomes immaterial. This allows one to ignore bound water and exclude effects from fiber swelling. The corresponding process considering

competition between two metals is

$K_M = [MR_a]/([M^{a+}][R^-]^a)$

$K_N = [NR_b]/([N^{b+}][R^-]^b)$

In this case, the selectivity coefficient $K_N^M$ is the quotient of the two formation constants adjusted for stoichiometry.

$$\frac{K_M}{(K_N)^{a/b}} = K_N^M = \frac{[MR_a][N^{b+}]^{a/b}}{[NR_b]^{a/b}[M^{a+}]}$$

where M and N are now the two metals, and a and b are their assumed valencies and corresponding stoichiometries. Although the concentration of dissociated anionic sites always cancels in this approach, the concentration issues of the bound (absorbed) and free solution ions only cancel for a = b.

Choice of concentration units can be Molarity, Molality, or ionic fractions. The numerical value for the selectivity coefficient is dependent on the choice of concentration. There are two common conventions for concentration scales, use of molal scales for both the solution and resin, assuming some state for pore liquid in the resin, or using a molal scale for the solution and ionic fraction (rational scale) for the resin. Using ionic fraction for the resin simplifies the mass balance equation for the resin, and has been selected for this study. The advantages of the selectivity coefficient is that it can describe the metal absorption isotherms, and allows for factors such as complex formation in determining selectivity of one metal over another. With appropriate considerations, the selectivity coefficient can be used to determine the thermodynamic equilibrium constants for ion exchange, which should be readily incorporated in Free Energy Minimization programs for predicting equilibrium metals distributions.

The disadvantages of the selectivity coefficient are

1. The use of several concentration bases for determining selectivity coefficients makes it more difficult to use values collected from multiple sources.
2. The assumption that anions are effectively excluded from a cation exchange resin is only accurate at low concentrations. At high concentrations (above the nominal 0.02 Molar ionic strength of the wood fiber), all ion exchange sites can be assumed to be occupied, and the conditions that maintain anion exclusion are negated.

## PRIOR YEARS RESULTS

Efforts in FY 96/97 established that the selectivity coefficient method provided a reasonable fit to the experimental data. Pulp, ion exchanged to the calcium form, was subjected to a series of acid wash experiments at various pH. After 30 minutes, the pulps are filtered onto a Buchner funnel and pressed between blotters to 90 psig. The sheets are then dried and analyzed for the metals of interest.

Taking the log of the selectivity coefficient equation,

$$K_H^{Ca} = \frac{[CaR_x][H^+]^x}{[HR]^x[Ca^{2+}]}$$

$$Log(K_H^{Ca}) = Log\left(\frac{[CaR_2]}{[Ca^{2+}]}\right) - xLog\left(\frac{HR}{H^+}\right)$$

This can then be rearranged to the point/slope formula for a straight line. Plotting the analytical results as $\log[CaR_2]/[Ca^{2+}]$ relative to $\log[HR]/[H^+]$, the data is fit to a straight line using a least squares linear regression. The slope of this regression is the exponent of the terms on the X axis in the selectivity coefficient (a/b), and the zero intercept is -Log K.

The result for calcium at pH ranging from 1 to 7 is given in Figure 2. For this case, $K_H^{Ca}$ ranges from 10 to 80, depending on the model used. The coefficient on protons is surprising. From the assumed equilibrium, the exponent on H and HR should be 2. A much better fit is obtained with an exponent around 0.6. Using a value of 0.61 for the exponent, the selectivity coefficient for Ca displacement with protons is $K_H^{Ca} = 10$.

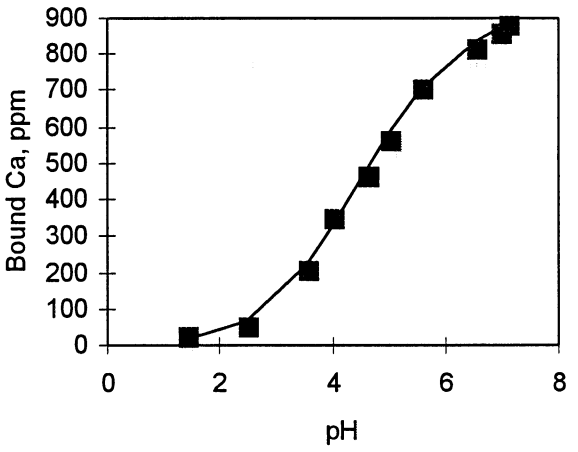



Figure 2. Bound calcium calculated relative to observed bound calcium.

The reason for the deviation from theory is not due to a different stoichiometry for the ion exchange process. Based on the number of acid sites in the pulp, each calcium neutralizes two sites as expected.[20] The deviation from theory has been attributed to the presence of different acid groups.[8] Laine reports that up to 1/4 of the acid groups present in an unbleached pulp are not glucuronic acids and are associated with lignin with a pKa around 5.4.

To evaluate surface effects, several experiments were carried out with increased ionic strength to suppress the electrical double layer and reduce capacitance. Using 1 M NaCl, the bound calcium was displaced by sodium at all pH levels. Similar experiments with sodium contents of 0.1, 0.01 and 0.001 M and magnesium contents of 0.01, 0.05, and 0.001 M all showed partial displacement of Ca, emphasizing the competition of the metals for the pulp binding sites. This provides a mechanism for the observed sharpening of the pH titration of pulp under higher ionic strength. This affect has previously been attributed to the influence of the electrical double layer and other surface related phenomena. However, from an equilibrium perspective, increasing the ionic strength increases the cation competition for the acid sites with the result that at any pH, more sites are occupied by the metal (in this case sodium) and fewer are neutralized by protons. The result should be a drop in initial solution pH, and a titration that behaves more like a solution equilibrium because the ion exchange continues to drive the protons into solution ahead of the titration.

Additional experiments evaluated equilibration times of 30 minutes and 120 minutes and noted no significant difference in bound metal content between the two reaction times. A 30 minute reaction time was established for all subsequent experiments.

## FY 97/98 RESULTS

Experimental work during the current fiscal year has carried out metal competition experiments and determined room temperature selectivity coefficients for $H^+$, $Na^+$, $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, and $Mn^{2+}$ (Table 1). Experiments carried out using a linerboard grade softwood (Georgia TIP[3] project 4153) have been found to be in agreement with the selectivity coefficients determined on the bleachable grade kraft softwood pulp. Similar experiments on a linerboard grade hardwood gave a significantly different response between protons and calcium, but metal competitions have given similar selectivity coefficients to the softwood work.

**Table 1.** Selectivity Coefficients. Format: horizontal is bound metal in the numerator, vertical is bound metal in the denominator. The value in brackets is the coefficient on the bound metal in the denominator. Values in bold are adjusted for activity coefficients.

| $K_{M2}^{M1}$ | | $M_1$ | | | | | |
|---|---|---|---|---|---|---|---|
| | | $K_{M2}^{H}$ | $K_{M2}^{Na}$ | $K_{M2}^{Mg}$ | $K_{M2}^{Ca}$ | $K_{M2}^{Mn}$ | $K_{M2}^{Ba}$ |
| | $K_{H}^{M1}$ | 1 | | | 10 (0.61) | | |
| | $K_{Na}^{M1}$ | | 1 | **0.4 (2)** | 1 (2) | | 0.5(2) |
| $M_2$ | $K_{Mg}^{M1}$ | | 2.5 (2) | 1 | **3** | 0.56 | 0.9 |
| | $K_{Ca}^{M1}$ | 0.1 ((1.6) | 0.10 | **0.3** | 1 | 0.56 | 0.9 |
| | $K_{Mn}^{M1}$ | | | 1.8 | **1.8** | 1 | |
| | $K_{Ba}^{M1}$ | | 2(0.5) | 1.1 | 1.1 | | 1 |

On-going efforts are:

1 to incorporate activity corrections into the selectivity calculations.

2. to extend the capability of the model to predict metal contents at solution ionic strengths exceeding the nominal ionic strength of the fiber and bound water.

3. determine selectivity coefficients at 40° and 60° C and develop suitable Gibbs Free energy expressions.

The measurement of the selectivity coefficients is discussed in detail in the 1997 Annual Program Review document, and Institute Technical Report on Project F017 (January 13, 1998) and will not be covered in great detail here. A version of Table 1 appears in the Institute Technical

Report. The values in that report are not corrected for activities. The values listed here are entered in bold if they do include solution activity coefficients in the calculation.

**Ion Exchange Sites**

Ion exchange sites (acid group content) have generally been determined from the metal analysis assuming calcium and magnesium (divalent metals) account for two acid sites,[20] and sodium a single site. This was convenient in that it did not require additional experimentation and the number of acid sites actually involved in ion exchange was of greater importance than the number observed by other methods. A similar procedure was established and validated by Wilson.[20] Using this method, the pulp averaged 54.9 meq/kg acid sites with a standard deviation of 4.2 meq/kg. However, this is not the industry standard procedure for measuring acid groups, and has the disadvantage that the pulp has to be put through the ion exchange procedure and analyzed for metal content. Several experiments were carried out analyzing the linerboard hardwood and softwood using the conductivity method[21] and the ion exchange method. This experiment also evaluated the effect of fines on this titration. The results are presented in Table 2.

**Table 2**: Acids by conductivity and by Ion Exchange (meq/kg)

| | SW, with fines | SW, w/o fines | HW, With fines | HW, w/o fines |
|---|---|---|---|---|
| **conductometric** | 88 | 100 | 115 | 111 |
| **conductometric** | 84 | 130 | 124 | 116 |
| **ion exchange** | 78 | 110 | 49 | 111 |
| **ion exchange** | 34 | 106 | 67 | 115 |

Although there is clearly a problem with the pulps containing fines, the pulps with the fines removed give good correlation between the two techniques. The pulp samples with fines did not give reproducible metals contents and could not be analyzed effectively for selectivity coefficients. In one experiment, the concentration of acids groups (as measured by bound metal content) varied between a low value of 34 meq/kg to a maximum value of 78 meq/kg. This is assumed to be due to an inability to collect a representative sample of pulp when fines are present, but needs further study.

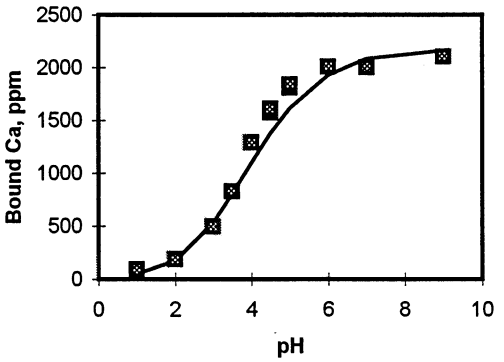



Figure 3. Linerboard data fit to previous selectivity coefficient.

**The Effect of Pulp Type**

The majority of the effort has been carried out on a bleachable grade kraft softwood produced in the laboratory from southern pine chips. Several duplicate experiments have been carried out on a commercial linerboard grade southern pine pulp. In Figure 3, the bound calcium results for the ion exchange experiments on the linerboard pulp are shown relative to calculated bound calcium

levels using the selectivity coefficient determined from the experiments on the bleachable grade softwood. Although the data has a sharper transition than the selectivity coefficient derived from the earlier data, the error is relatively small. An improved fit is possible, but is not necessary, which suggests that one set of selectivity coefficients will be applicable to other pulp samples.

For hardwoods, the acid removal of calcium did not follow the softwood model (Figure 4). Using a linerboard grade southern hardwood, the best fit gave $K_H^{Ca} = ([CaR_2][H^+]^{1.5}/([HR]^{1.5}[Ca^{++}]) = 0.01$. This is much closer to the theoretical response (a coefficient on protons and bound hydrogen of 2). Because of the difference in the coefficient terms (0.61 for softwoods, 1.5 for hardwoods) it is not possible to compare the selectivity coefficients directly. However, the transition from the bound calcium state to the bound proton state occurs right around pH 4 for both pulps. The difference is that the softwood transition is quite brood, and the hardwood transition is sharp, similar to the type of pH transition normally encountered in solution chemistry.

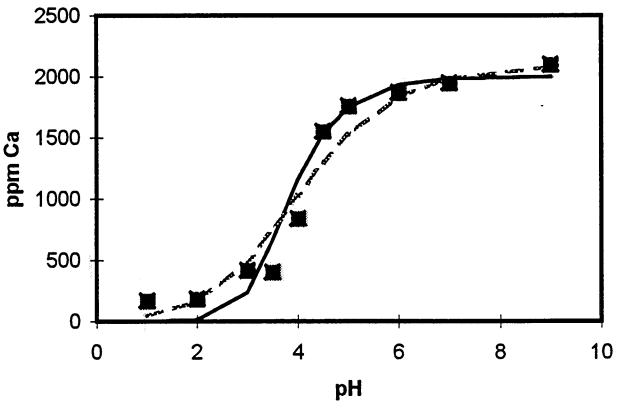



Figure 4. Calcium removal with acid for a hardwood pulp. Dashed line is K =10, s = 0.61, solid line is K = 0.01, s =1.5.

The equation listed above fits the data rather closely for the pH region above 4. It overestimates the bound calcium content in the pH 3 to 4 region, and underestimates the bound calcium below pH 3. This error is due to a displacement of the response curve at about 500 ppm residual calcium. Using a selectivity coefficient of 0.0001 and coefficient on bound and free protons of 2 (as predicted from stoichiometry) also gives a good match to the experimental data, down to the pH of 3 where it significantly underestimates the residual bound calcium. This result has been observed quite frequently when divalent cations are replaced with monovalent cations as is seen also in Figure 5.

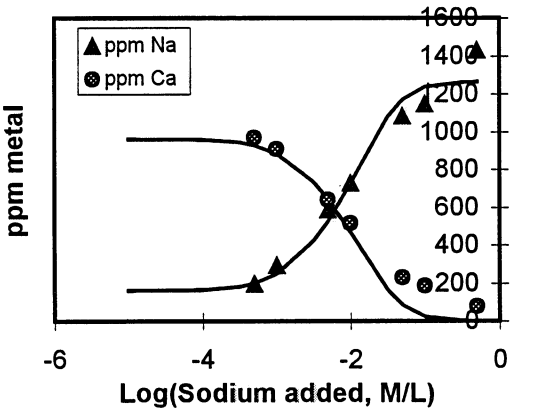



Figure 5. Replacement of calcium with sodium.

**Deviation from Theory**

Laine, has proposed that there are two different carboxylic acid groups in wood pulps, the glucuronic acid groups with a pKa of 3.3, and a second group associated with lignin and with a pKa around 5.4. Using $^{13}C$ and $^{31}P$ nmr, two groups[22,23] report lignin acid contents ranging from 0.18 to 0.4 mmole per gram of lignin corresponding to 10 to 20 mmole per kg of pulp. This is slightly less than the estimates made by Laine.[8] The deviations observed in the

proton and sodium experiments are supportive of the Laine concept of two different acid groups. However, we would expect the second acid group with a higher pKa would release calcium at higher pH, and the error would be to overestimate the bound proton level in the pH region 4 to 5.5.

The assumption that all the lignin acid groups represent one localized structure with a single or closely related pKa's is unlikely and the pKa of 5.4 is unusually high. Most benzoic acids and hydroxy propanoic acids display pKa's well below this range. This data indicates there is a tightly bound form of calcium and is more consistent with the concept that some acid groups are in close enough proximity to have an inductive effect on the second acid dissociation. For example, the dicarboxylic acids from $C_3$ (Malonic Acid) to $C_7$ (Pimelic acid) and all the cyclohexane-dicarboxylic acids (except 1,1) have a pKa for the second acid dissociation above 5.4.[24] This explanation would have a chelate affect on divalent cations. The hardwood data suggests that about 25% of the acid sites fall into this category, and the softwood data in Figure 5 places suggests about 15% in this category. Both numbers are within the range reported by Laine.[8]

**Bound Water**

Adjusting for the bound and free water remaining in the fibers has presented a problem throughout the early phases of the analysis. The initial assumption was that all water should be treated as free water, and the metals analysis were adjusted by subtracting the amount of metal that would be contained in an equal amount of external water. It soon became apparent that this was a poor assumption as is obvious from Figure 6. In this experiment, magnesium was used to displace bound calcium. At a molar concentration of 0.01 M $MgSO_4$, the adjusted bound magnesium content is less than the calculated bound magnesium content at 0.001 M $MgSO_4$. At 0.1 M, both the adjusted bound magnesium and adjusted bound calcium are negative.

This assumption was abandoned, and for simplicity, it was assumed that all water remaining after pressing the pulp at 90 psig was bound water, subject to anion exclusion and unable to solvate cations. Typically, the fibers contained 1.1 to 1.3 grams of water per gram of pulp after pressing. Since this is in the same range as typical fiber saturation points (as defined by Scallan),[25] it seemed a safe assumption that this water was closely associated with the fiber. This assumption proved adequate for the majority of the data collected. However, in many cases, the experiments carried out at the highest displacing metal concentration showed significant deviation from the relationship predicted by the selectivity coefficient. This typically occurred between 0.005 and 0.01 Molar in metal, concentrations common to extraction stages and brown stock washing.

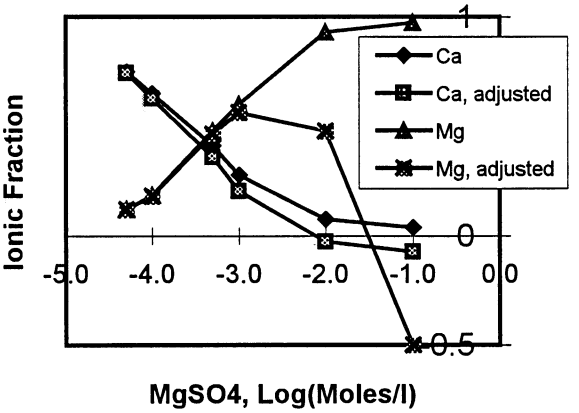



Figure 6. Mole fraction of calcium and magnesium assuming remaining water is bound, or bulk water.

Several possibilities were considered for the deviation from ideal behavior:

1. The bound water assumption is incorrect
2. Once the external solution ionic strength exceeds the ionic strength of the fiber and bound water, the conditions for anion exclusion no longer exist, and the fiber can begin to absorb both anions and additional cations.
3. The added metal has reached a concentration where it can compete against protons for other, high pKa acid sites such lignin phenols.

Since the first item is an assumption, that all water remaining after pressing at 90 psig is bound water, it was the first to be tested.

**Table 3**. Estimates of free and bound water in fibers from metal analysis

| Metals | Conc. (M/l) | Analysis (ppm) | Calculated (ppm) | Difference (ppm) | solution (ml) | wet fiber (g) | bound water (g/g) |
|---|---|---|---|---|---|---|---|
| Ca, Mn | 0.01 | 2,045 | 1,592 | 453 | 0.825 | 2.06 | 0.23 |
| Ca, Mn | 0.05 | 4,230 | 1,689 | 2,541 | 0.925 | 2.07 | 0.15 |
| Ca, Mn | 0.5 | 26,250 | 1,728 | 24,522 | 0.893 | 2.16 | 0.27 |
| Mg, Na | 0.05 | 2,000 | 1,389 | 611 | 0.531 | 2.11 | 0.58 |
| Mg, Na | 0.5 | 12,000 | 1,462 | 10,538 | 0.916 | 2.14 | 0.22 |
| Ca, Mg | 0.1 | 2,357 | 783 | 1,573 | 0.648 | 2.05 | 0.40 |
| Mg, Ba | 0.01 | 4,184 | 3,152 | 1,032 | 0.752 | | |
| Mg, Ba | 0.1 | 14,642 | 3,279 | 11,363 | 0.828 | | |
| Average | | | | | 0.81 | | |

The error introduced from bound and free water is small at low metal concentrations, but becomes large at high concentrations as observed in Figures 6 and 7. To evaluate assumption 1, several sets of experiments were carried out containing experiments at the high concentrations where the error is encountered. The selectivity coefficient was determined using the data at low ionic strength. The amount of water required to balance the analysis was then determined, assuming the free water of the internal solution was at the same metal concentration as the surrounding solution. The data for four such experiments is summarized in Table 3. These results suggest that nearly all the water in the fiber is available to solvate ions. The approximately 0.25 g of water that is not available is presumably water of hydration of the ionic groups, and directly associated with polar sites in lignin and cellulose.

Berthold defines the water adsorbed to pulp in three categories, non-freezing, freezing and free. Non-freezing water is the water directly adsorbed or associated with polar sites of the cellulose and lignin. Freezing water is more loosely associated with the fiber, but the melting point is depressed below 0° centigrade. Free water is in the pores of the fiber and freezes at zero.[26] Berthold contends there are about three absorbed waters per sugar monomer (one for each free OH group), and 5 to 7 waters for each absorbed cation. The total comes to about 0.3 g/gram of fiber, a value supported by other research as well.[27] The 0.25 g found to be excluded in these experiments is in the range indicated by Berthold as non-freezing water, and by Stamm as the fiber

saturation point.

This result raises questions about the earlier experiments shown in Figure 6. Resent work, repeating the Ca/Mg matched the earlier results quite closely, except for the data at 0.1 M Mg, which was over three times the "bound" magnesium content of the earlier experiment (Figure 7). One difference in the two experiments is that the anion in the initial experiment was sulfate where the anion in the most recent experiment was chloride. Divalent anions are affected more strongly by the charge on fibers and are more efficiently excluded than monovalent anions. This may be the source of the apparent discrepancy in the two data sets.

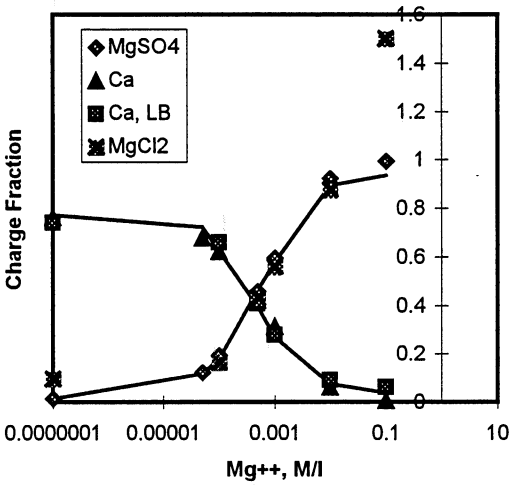



Figure 7. Mg experiments using $MgCl_2$ and $MgSO_4$. For graphing purposes, the bound Mg at 0.1 M has been reduced from a charge fraction of 3.5 to 1.5.

**Equilibration time and Kinetics**

A concern arose about the length of time required for the samples to reach equilibrium when it was learned that Rorrer (OSU) was using longer retention times in similar experiments.[28] A second equilibration time experiment was run, this time using the linerboard grade hardwood pulp. The experiments were carried out on pulp ion exchanged to the calcium form and containing an initial calcium content of 1900 ppm. Experiments were at room temperature and pH 3.5. Retention times of 5, 15, 30, 45, and 90 minutes were tested. The calcium content of these pulps was found to be 504 ppm, 494.5, 496.5, 497.5, and 438 ppm respectively. Since there was no consistent change in calcium removal after 15 minutes, the 30 minute and 45 minute reaction times used in the project are sufficient to insure equilibrium. It is assumed that the low calcium content observed at 90 minutes is either experimental error, or possibly slow conversion of acids to lactones under the mildly acidic conditions. This experiment needs to be carried out one more time using two metals in the exchange process, but all indications are that the exchange is quite rapid, and a closer inspection of the Rorrer data suggests they reached

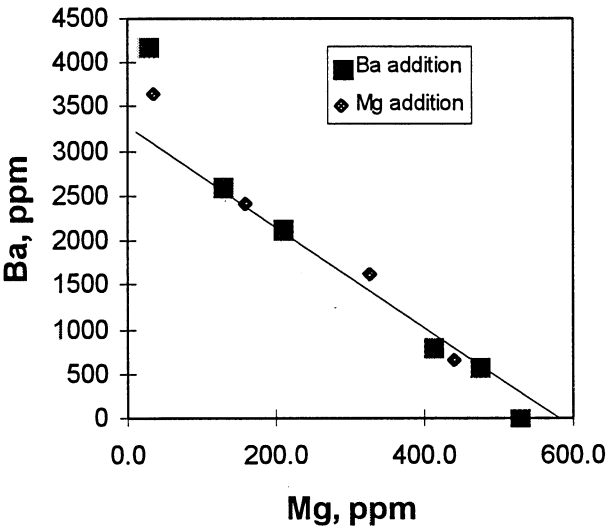



Figure 8. Fit of data to predicted concentrations is good when both metals are added.

equilibrium within about a half hour as well.

### Validation

As an initial test of the method, several additional cases were included in the magnesium and barium experiments. The selectivity coefficient was determined using the standard procedure with barium added to solution and displacing magnesium. In four extra experiments, both magnesium and barium were added to solution. These results are displayed in Figure 8, where the points represent the analyzed magnesium and barium content of the pulp, and the straight line the calculated equilibrium. The large squares are the data for the added points that were not part of the measurement of the selectivity coefficient. The selectivity coefficient has successfully estimated the bound magnesium and barium under all conditions except solution barium contents greater than 0.01 moles per liter, where the method is known to break down.

## CONCLUSIONS

Selectivity coefficients have been calculated for the partition between solution and fiber for Ca, Mg, Mn, and Ba in binary metal competition experiments. The technique is accurate for solution concentrations up to about 0.01 molar at which point the ion concentration in solution exceeds the ion concentration in the fiber. Indications are that this can be modeled by assuming that all but 0.3 grams of water per gram of fiber is available as free water. For the monovalent and divalent cations evaluated, the exchange stoichiometry is close to prediction based on equal anionic and cationic charges in the fiber. However, for the case of acid competition with calcium, it has been necessary to adjust the exponent on bound and solution protons in the selectivity coefficient. This is thought to be due to the presence of acid groups in close proximity where there is an interaction that affects the pKa's. This also explains a deviation of the calcium exchange with sodium at low bound calcium levels.

## PROGRESS ON FY97 GOALS

1. Room temperature selectivity coefficients (completed).
2. Evaluated temperature selectivity coefficients (on schedule).

## REMAINING WORK

1. Complete re-calculation of all selectivity coefficients, including incorporation of activities and free water adjustments.
2. Evaluate the influence of temperature on selectivity coefficient, and determine the thermodynamic equilibrium constants and Free Energy for the ion exchange reactions.
3. Evaluate the influence of phenolic groups and high pH on the ion exchange.

# EXPERIMENTAL

**Pulp Preparation (Ca Case)**
Pulps are fractionated on a 100-mesh screen to remove fines. The pulp is then acid washed twice at pH 1.5 and 70°C for 90 minutes. The pulp is adjusted to pH 7.0 and set over night to hydrolyze lactones. It is soaked in 0.01 M $CaCl_2$ and the pH adjusted to 8.0. The metal exchanged pulp is washed thoroughly with nano-pure water (Resistivity > 17 MΩ), leached over night in nano-pure water, and thickened to 20% consistency on a Buchner funnel. It is then fluffed and placed in bags for storage.

**Ion Exchange Procedure (Acid Exchange)**
Experiments were carried out by diluting 10 OD grams of pulp to 1 liter with either nano-pure water, or a solution of nano-pure water containing the competing metal. The pH was adjusted to target with hydrochloric acid, or sodium hydroxide, and the sample mixed for 30 minutes using a U-shaped polypropylene stirrer. The sample was dewatered on a Buchner funnel and the pulp pad pressed to approximately 50% consistency using the TAPPI handsheet press set for 98 psi. Pressed pulps were weighed so the metals content could be adjusted for dissolved metals.

**Ion Exchange Procedure, Metal Competition**
Metal competition was carried out by suspending 10 OD grams of pulp (ion exchanged to one of the two metals of interest) in 1 liter of nano-pure water, containing a known Molarity of the second metal as a soluble salt. A typical set of experiments tests 5 or 6 molarities ranging from 0.0001M to 0.1 molar. For all experiments to date, pulps were adjusted to pH 7 with sulfuric acid or sodium hydroxide, and were stirred at room temperature for 30 minutes. Pulps were then filtered onto a clean Buchner funnel and pressed between blotters at 98 psig.

Pulps were dried at 105°C; digested in nitric acid, hydrogen peroxide, and hydrochloric acid; and analyzed by ICP Emission Spectroscopy.[29] Filtrates are analyzed, on a spot basis and have shown no significant deviation from calculation by difference..

**Calculations**
All pulps were analyzed for sodium, magnesium, calcium, barium, manganese and iron. The metals of interest (the starting metal, and exchanging metal) were converted to ionic fraction basis by converting ppm to moles per 10 g. This value times the valence (to account for the charge) divided by the starting number of acid sites per 10 grams gives the ionic fraction (fraction of acid sites neutralized by the metal). Free metal was usually taken as the difference between the starting concentration and measured concentration for the starting bound metal, and added metal less bound metal for the exchange metal. The free metal concentrations have also been analyzed in several experiments and do not vary significantly from the calculated values.

## ACKNOWLEDGMENTS

Technicians Alex Shaket, Narendra Patel, and Alan Ball have all contributed to the experimental work of the project and I am grateful for their effort and diligence in conducting the experiments. I would like to thank the members of the Chemical Pulping Project Advisory Committee and Dr. Earl Malcolm for periodic reviews of the project and helpful discussions in establishing and refining the experimental approach. I need to thank Dr. Paul Wollwage (Weyerhaeuser Corp.) who initially brought up the problem with lactones. Funding for this project is provided by the Member Companies of the Institute of Paper Science and Technology. This project is significantly enhanced by parallel work on Georgia TIP$^3$ PP98-MP1 (IPST project 4153) and I thank Clark Woitkovich for including me in this project and the additional finical assistance it provides.

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# Metals Management in Low Effluent Pulp and Paper Mills

Georgia Traditional Industries Program
in Pulp and Paper

6 Month Progress Report

to

**The Member Companies of the Institute of Paper Science and Technology**

March 4, 1998

Alan Rudie
Associate Professor, Chemistry

## SUMMARY:

Key Words: Closed mill, Non-process elements, transition metals, alkaline earth metals, scale, bleaching, water reduction.

Many Georgia mills are attempting to reduce water usage and effluent volumes either because the mill has outgrown the existing water supply or to comply with stricter environmental regulations. Regardless of the incentive for reducing water use, increased internal recycle of water increases the build up of contaminants in the mill water system.[1,2] At high levels, these non-process materials have an adverse impact on the process, reducing brightness and increasing bleaching costs,[1] scaling process equipment, and increasing corrosion.[2] All of these issues have presented problems in Georgia mills with relatively open water systems. They are becoming even more troublesome as mills reduce discharge levels further. This research proposes to evaluate the behavior of the Alkaline Earth metals: Magnesium, Calcium, and Barium and first row transition metals Manganese, and Iron with bleached and unbleached pulps. The proposed approach is to determine fundamental properties of the metals, oxidation state, the local coordination environment, and binding constants for metal coordination to pulp. Specific objectives and the status are as follows:

## PROJECT OBJECTIVES and STATUS:

1. Determine formation constants for Mg, Ca, Ba, and Mn with wood pulp (IPST). **Status:** *Room temperature binding constants have been measured for Na, Mg, Ca, and Mn. Task ahead of schedule.* (Note, task not offered as matching funds)
2. Determine the coordination environment of Ca, Mn, Fe and tightly bound Fe in wood pulp using XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy (SREL). **Status:** *Initial X-ray analysis indicates the binding environments for calcium and hard to remove iron are sufficiently uniform to be characterized. The binding environment for tightly bound iron has been characterized and matches the 3-methoxy-4-hydroxy site of lignin guaiacol. Task on schedule.*
3. Confirm the coordination environment of Ca, Mn and Fe using model compounds (IPST), XANES, EXAFS (SREL) and X-ray Crystallography (GT). **Status:** *Synthetic work has begun to prepare complexes of Fe(III) with guaiacol, and Fe(II) with vanillin. Task on schedule.*
4. Identify methods for removing tightly bound iron (IPST). **Status:** *No progress.*
5. Evaluate the influence of tightly bound iron on ozone and peracetic acid bleaching (IPST). **Status:** *Task starts in FY 99.*
6. Evaluate re-absorption of metals on pulp, both from the fundamental perspective and as a means of controlling metals build up in the process. **Status:** *Task starts in FY 99*

# Metals Management in Low Effluent Pulp and Paper Mills

## BACKGROUND

Georgia mills are struggling to reduce water use to minimize saltwater incursion into the Georgia Florida Aquifers and reduce waste water discharges to surface waters. Accomplishing this task requires mills to reuse waste water from one unit operation in other areas of the mill that have less stringent requirements for water purity. The additional water recovery increases the recycle and accumulation of undesirable materials in the mill. These unwanted materials and the problems they create can be categorized as follows:

Surface active materials (anionic trash): These materials include clay, talc, silicates and fines. They interfere with wet end chemistry and consume alum or cationic polymers used as retention aids. They can also reduce sheet brightness, alter sizing and participate in deposit formation in the wet end.

Pitch: It is difficult to separate pitch and surface active materials, because pitch is surface active and surface active materials participate in deposits. Pitch materials include natural wood resins like fats, fatty acids, resin acids and terpenes, and polymers like surfactants, defoamers and latex. These materials initiate deposit formation in the wet end, dryer section and calender stacks and elsewhere in the mill.[2]

Non-Process Elements (NPE's): NPE's are (generally) non-organic materials that enter the mill with wood, water or as trace materials in process chemicals. They often accumulate in various areas of the mill and can cause scaling, fouling and dead load problems. They can be categorized into alkali soluble and alkali insoluble groups.[3] Soluble elements include potassium and chloride. Because they are soluble under nearly all conditions and do not readily form stable complexes, these elements end up in the recovery cycle and accumulate as dead load in the green and white liquor.[3,4] They have a greater tendency to fume than sodium and sulfates so they also accumulate on boiler tubes and increase tube fouling rates and tube corrosion.[5] Alkali insoluble metals include Mg, Ca, Ba, and all the first row transition metals. They all have high affinities for the ion exchange sites in wood pulp and low solubility at high pH so they accumulate where acid filtrates are used on alkaline washers.[2,6] Mg, Ca and Ba all contribute to scale in the bleach plant, the liquor heaters and extraction screens in the digester[7] and the evaporators. The transition metals are usually found in much smaller amounts but can affect brightness and interfere with oxygen based bleaching methods.

This project is focused on understanding the behavior of the alkaline insoluble metals. It is concerned with characterizing the local environment of the metal binding sites and equilibrium behavior of metal binding. The project will also investigate the effect of tightly bound iron on totally chlorine free bleaching and the potential for a secondary metals accumulation between the second acid bleach stage and preceding alkaline extraction stage of the bleach plant.

## Metal Binding

The alkali metals and first row transition metals absorb in wood pulp under neutral and alkaline conditions, and are released by the pulp under acidic conditions. The transition from the bound state to the dissolved state is centered around pH 4 and is usually ascribed to carboxylic acid functional groups which have a pKa in this range.[8,9,10] However, the presence of carboxylic acid groups in wood pulp and the pH sensitivity of the metal binding behavior are not conclusive evidence that this is the binding site for metals in pulp. The Donnan approach, advanced by Towers and Scallan, assumes the cations are dissolved in the internal solution, and not bound to the acid groups at all.[10] Certainly, above pH 8, lignin phenolic groups start to contribute to the anionic group content of the fibers, begin to attract cations on the same basis as any anionic site and probably provide specific binding sites for some metals. For example, there is good evidence that both iron and calcium[11] form complexes with quinone/catechol sites and other lignin functional groups. [12]

What is needed:

1. A thorough understanding of metal binding to pulp including binding sites and relationship to pulp source and lignin content.
2. Accurate "equilibrium" models capable of predicting the behavior of the alkali insoluble metals in the fiber line. These must have a high level of accuracy in the typical acid bleach range between pH 1.5 and pH 4 used in chlorine dioxide and peracetic acid bleaching.
3. Improved metals removal strategies that will reduce the carryover of tightly bound iron and wash losses of acid soluble metals into the later stages of the bleach plant.
4. An improved understanding of how the residual metals will behave in the later stages of the bleach plant under various wash water recirculation strategies and final bleach stage pH's.

Item 2 above has been the subject of several research efforts and will be discussed more fully below. Items 1 and 3 have taken a back seat to research on the initial metals removal process and item 4 has received very little attention, because it is not a problem until mills succeed in recovering filtrates from the initial stages of the bleach plant. Assuming current efforts do succeed, the nature of the wash water recirculation strategy, efficiency of the metals removal process and end pH of the acid bleach stages will control how much metal is carried through to the final stages of the bleach plant and how much is recycled into the brown stock area. To avoid the cost of a second NPE control system, the metals control in the later stages of the bleach plant will be limited to by-passing the alkaline washers and pH control.

Of particular interest is the behavior of iron which does not abide by the more typical ion exchange behavior observed for the monovalent and divalent metals. Iron generally has a starting concentration around 30 ppm in brown stock pulp. Acid washing at pH 1.5, or

treatment with DTPA will remove about 2/3rds of the iron, but around 10 ppm remains and cannot be removed without substantial pulp damage. This remaining iron has been called hard-to-remove iron, tightly bound iron and intractable iron, but beyond the distinctive titles, it has been largely ignored and generally considered inactive. However, one group has investigated the tightly bound iron and concluded that it does reduce the efficiency of peroxide bleaching.[13] In addition, if iron is bound to lignin, it will be released as delignification progresses. Then it is free to build up and interfere with the later stages of bleaching. Removing tightly bound iron should increase TCF (totally chlorine free) bleaching efficiency and may be critical to preventing problems with iron accumulation in the later stages of the bleach plant. Since removing this residual metal has resisted all conventional approaches, it becomes imperative that we improve our understanding of what contributes the unique stability to this binding site.

**The Metal Binding Site**

Attempts to determine the nature of metal binding sites are hindered by low concentrations (typically 30 ppm for iron up to 1000 ppm for calcium), and the variability and non-uniformity of the substrate. These metal concentrations are generally below the detection limits of conventional spectroscopy (UV-VIS, IR, nmr) and sources of the majority of the binding sites (hemicellulose and lignin) make it difficult to perform meaningful experiments with a model substrate at higher concentrations.

Techniques that probe the metal site directly have a better chance of success. Of most interest for this project are several X-ray techniques capable providing useful information at low metal concentrations. X-rays are energetic enough to eject core level electrons from the metals of interest. Since the required X-ray energy is somewhat unique for each element, there is generally less interference from other elements, and almost no interference between the transition metals and the low z carbon and oxygen background material in wood pulp. X-ray absorption and fluorescence techniques can provide information on the abundance and distribution of trace metals in the sample. The XANES (X-ray Absorption Near Edge Spectroscopy) provides information on metal oxidation state and to some extent symmetry.[14] In this technique, the X-ray source is diffracted by a silicon oxide crystal to obtain near monochromatic X-rays. The X-ray energy is then scanned across the absorption edge for the metal of interest. The X-ray energy required to eject an electron from the metal is sensitive to number and distribution of the valence electrons in the metal. The presence of low lying unoccupied orbitals usually give rise to a number of low intensity pre-edge features and these contain some information on symmetry and the distribution of valence electrons.

The EXAFS (Extended X-Ray Absorption Fine Structure Spectroscopy) technique sweeps the X-ray spectrum of the edge to about 200 eV above the edge.[14] Slight variations in absorptance or fluorescence intensity are due to the proximity of other atoms in the coordination sphere of the metal. The EXAFS technique is capable of probing the metal environment out to about 4 to 5 Å distance from the metal nucleus and provides information on the type and number of atoms and their radial distance from the metal

nucleus. A limitation of the XANES and EXAFS techniques is the need for a wide range in radiation wavelengths and the high radiation losses experienced in selecting for a narrow band of energies. These techniques require very intense X-ray sources, and can only be carried out at the few synchrotron facilities where X-ray beam energies and intensities are sufficient for this application.

This project proposes to use the XANES and EXAFS techniques to determine the oxidation state and local coordination environment of metals in wood pulp. Metals suitable for X-ray analysis include Ca, Mn and Fe and Ba. Since barium is very near or beyond the minimum concentration limits of current equipment and there is no reason to believe that it's binding environment would differ from calcium, it has not been included in the project.

**The Metal Binding Equilibrium**

Trace metal binding to wood pulp has been modeled using solution equilibrium theory, Donnan equilibrium theory, and a modification of solution equilibrium theory known as the Selectivity Coefficient. In all cases, the fiber is assumed to carry a negative charge associated primarily with carboxylic acid functional groups.[8,9] In solution equilibrium, it is assumed that the acid group dissociation is dictated by the pKa, and an appreciable number of free anions exist. It is also assumed that the ion exchange sites are uniformly dispersed in solution. The theory ignores the difference in acid group concentration in the fiber relative to the solution, and the variation in acid group concentration from fiber swelling and shrinking.

As applied to wood pulps, Donnan theory is not concerned with the nature of the charge groups. The cations are attracted to the negative charge on the fiber caused by dissociation of a relatively few acid groups. The number of acid groups dissociated is considered rather small due to the principal of charge neutrality, that it is impossible to isolate a particle with an analytically measurable imbalance in anions and cations. The major factors controlling metal binding are fiber charge, cation charge, fiber swelling and solution ionic strength. As applied, this theory assumes the cations are dissolved in the water associated with the fiber and ignores any specific affinity between metals and binding sites in the fiber.[10] In the Donnan theory, all monovalent metals are assumed to behave the same and all divalent metals behave the same. In the more general development of Donnan equilibrium theory for semipermeable membranes, formation and acid dissociation are not ignored, but are handled as separate chemical equilibria.[15]

The Selectivity Coefficient also recognizes that relatively few acid groups are dissociated and the rest of the charged groups have to be balanced with protons or metal cations.[15] The basic theory is only valid at solution ionic strengths below the ionic strength of the charge groups in the fiber. The concentration adjustment for charge groups in the fiber, and changes in concentration due to fiber swelling and shrinkage are assumed to cancel out in the manipulation of the equilibrium equations. The theory recognizes specific attractions between metals and binding sites and accounts for the large differences

between monovalent and divalent metals as well as the smaller differences in absorption of different divalent metals. The uniformity of the three systems is that they all agree that the carboxylic acid functional groups contribute the majority of the acid groups available. The two ion exchange theories - Donnan theory and the selectivity coefficient - recognize that this may not be the specific binding site for the metal, the cations balance the charge but the cations may be dissolved in the swollen fiber or bound to another non-anionic site. The exact nature of the binding site remains unknown and is technically unnecessary for application of the theories.

Selection of a the most useful theoretical method is not just a case of accuracy. The most robust software to calculate chemical equilibria uses the Gibbs Free Energy minimization approach. This theory readily incorporates chemical equilibria, but may have trouble with the Donnan theory which uses a different mathematical approach. On the other hand, the selectivity coefficient can be considered as a simple ratio of two solution equilibrium expressions, and should fit nicely into the Gibbs free energy minimization method. Because the theory is designed to explain ion exchange phenomenon, the selectivity coefficient approach has inherent advantages over the conventional solution equilibrium approach and has been used in this project.

**Progress, July 1, 1997 to January 30, 1998.**

XANES: The iron XANES spectrum on several pulp samples had been collected prior to applying for the TIP[3] grant. It showed a gradual shift of the X-ray edge from iron (III) to iron (II). On a relative scale, the X-ray edge of the as received pulp is very close to the X-ray edge of the selected Fe(III) standard, ferric ammonium sulfate. Conventional bleaching (DED), acid washing and DTPA pretreatments all shift the X-ray edge about 3.5 to 4 eV to lower energy, about half way to the X-ray edge of the Fe(II) standard - ferrous ammonium sulfate. The presence of iron (II) in the system is surprising. There is reason to expect a reduction, iron reacts with the guaiacol structure to couple the guaiacols with iron (II) as the probable product.[16] The question is why it does not oxidize back to Fe(III) under the ambient storage conditions or why the bulk iron in the starting sample was not also iron (II). There are other possible explanations because the X-ray edge can also be sensitive to changes in symmetry of the coordination environment.

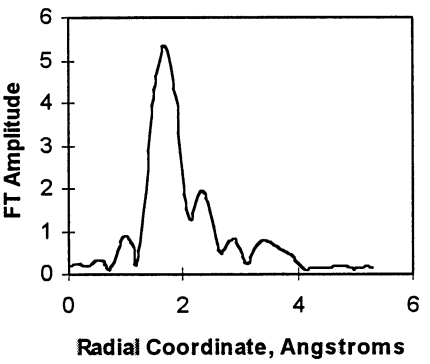


**Figure 1.** FEFF6 simulation of Fe-guaiacol.

Manganese XANES spectra were determined as part of this project. As expected, the manganese XANES spectrum gives an X-ray edge very similar to Manganese sulfate, a Mn(II) reference. It is shifted slightly to higher energy which may indicate a small amount

of Mn in a higher oxidation state, or differences in the coordination environment. The residual manganese in acid washed and chelated pulp was below the detection limit of the beam line.

## EXAFS

EXAFS spectra have been obtained for both tightly bound iron, and bulk calcium. Because of the low level of iron in the pulp, the EXAFS spectra were obtained as a two day extended series of 45 minutes scans and the scans were averaged to obtain a clean spectrum for analysis. The EXAFS radial distribution function (Figure 1) shows features at about 1.8, 2.3, 2.8, 3.4, 3.6 and 4.7 Å. Typically, the radial distribution function contains a phase shift of about 0.5 Å which cannot be fully accounted for until suitable model compounds have been studied. The presence of features out to 4.7 Å is a little unusual and an indication this is a fairly massive object.

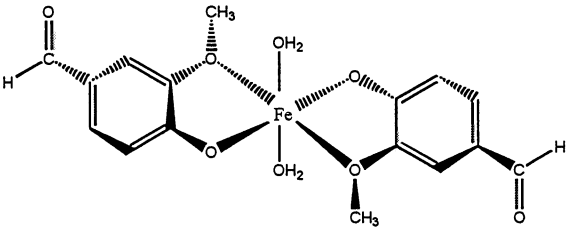


**Figure 2.** Iron guaiacol model.

Probable binding sites were thought to be the 1-2-hydroxy group of catechol (o-quinone) and the 1-hydroxy-2-methoxy group of guaiacol. Bond lengths and angles were estimated for Fe bonded to both a quinone and guaiacol and the structures drawn using the software ChemDraw. From this drawing, a second file was developed identifying each atom in the model and the x,y,z coordinates. The EXAFS spectrum of the model is simulated using the program FEFF6.[17] The results of the guaiacol model (Figure 3) matched the iron EXAFS spectrum almost identically out to 4 Å. This model does not produce the 4.7Å peak. Consideration of residual kraft lignin structures suggests the likelihood of a benzyl feature off of the C-5 carbon of the phenyl propane unit. If this aromatic ring orients perpendicular to the guaiacol group bonded to the iron, it would be positioned at 4.7 to 4.9 Å from the iron. This orientation would also have a blocking effect on the guaiacol oxide group, a possible source of the unique stability of the iron.

The calcium EXAFS is shown in Figure 3. The radial distribution function for this spectrum (Fig. 4.) has major features at about 1.8, 3.5, 4.2, and 5.6 Å. Again, the extended spectrum is a little unusual. The key candidates for theoretical modeling of this site are the carboxylic acid functional group of uronic acids. Carboxylic acids can attach either symmetrically, with both oxygens bonding to the metal, or asymmetrically with just one of the two oxygens bonded to the metal. Both options will need to be evaluated. Both o-quinones[11] and guaiacol also provide other possible binding sites for the calcium.

## Model Synthesis

The chemical modeling effort has concentrated on preparing a model of the iron guaiacol site. Efforts to synthesis chemical models of iron(III) with guaiacol and iron(II) with vanillin have thus far met with limited success. Iron(III) appears to react with phenols to initiate a coupling reaction as reported in the literature.[16] The resulting guaiacol oligomers contaminate any product obtained and make it difficult to isolate anything useful. Iron(II) reacts nicely with vanillin to give a yellow precipitate. Efforts to purify and recrystalize this material all resulted in a color change to red. Initially, it was thought that this was due to inadvertent oxidation of the complex to Fe(III). However, this color change was also observed when the product was simply dried *in-vacuo* suggesting it is a change in the coordination environment around the iron, associated with a loss in water. Efforts to recrystalize the red product are under way. Once suitable crystals are obtained, they will be characterized by X-ray diffraction and EXAFS. If this is a good match for the EXAFS spectrum of tightly bound iron, an effort will be made to prepare a similar complex with a 5-benzyl group to see if it produces the EXAFS feature at 4.7Å.

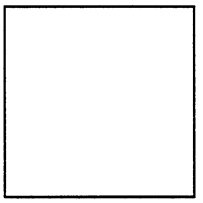

**Figure 3.** Calcium EXAFS

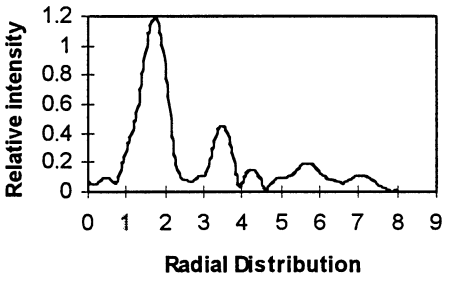


**Figure 2.** Radial distribution function for Ca EXAFS.

## Determination of Selectivity Coefficients

Selectivity coefficients have been measured for calcium relative to acid (protons), sodium, magnesium, and barium; barium relative to sodium and magnesium; and magnesium relative to manganese. The selectivity coefficient model for calcium removal by acid is shown in the following equation.

$$K_H^{Ca} = \frac{[CaR_2][H^+]^{0.61}}{[HR]^{0.61}[Ca^{2+}]}$$

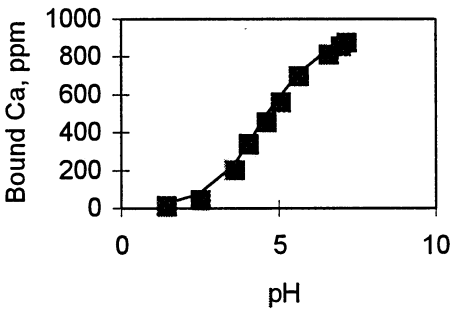


**Figure 3.** Calcium removal with acid.

The fit of the model (figure 5) to the data is excellent. However, the coefficient on protons and undissociated ion exchange sites is 0.61 instead of 2 as is expected from theory. The reason for this deviation from theory is subject to some debate. Laine et al.[18] suggest the deviation is due to the presence of two ion exchange sites with pKa's of 3.4 and around 5.5. There is some evidence from this work that the deviation is due to the close proximity of some acid sites to each other resulting in electrostatic separation of the pKa's.

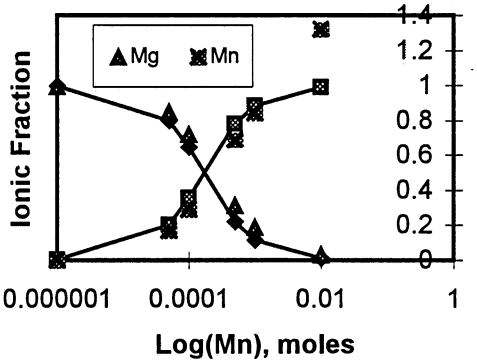


**Figure 4.** Displacement of magnesium with manganese.

Although the deviation from theory is disconcerting, it provides an accurate model of calcium absorption and removal by acid. Sticking strictly to theory and using a coefficient of 2 on the protons and associated acid groups produces a relationship with a much sharper step change from the bound to unbound state. This is not suitable for modeling because of the significant deviation observed in the pH 2 to 4 range. Hydrogen is the only cation evaluated so far that deviates significantly form theory. For example, replacement of magnesium with manganese (figure 6) has the appropriate 1 to 1 ratio with a selectivity coefficient of 1.8.

Room temperature selectivity coefficients have been determined for $H^+$, $Na^+$, $Mg^{2+}$, $Ca^{2+}$, $Mn^{2+}$, and $Ba^{2+}$. Expressed as the selectivity of calcium against the other cations, they are:

$K_H^{Ca} = 10$, $K_{Na}^{Ca} = 1$, $K_{Mg}^{Ca} = 3$, $KMn_H^{Ca} = 1.8$, $K_{Ba}^{Ca} = 1.1$

The coefficients are all 1 for the divalent metals, is 2 for competition between calcium and sodium (the RNa and $Na^+$ terms are squared) and 0.61 for competition between calcium and hydrogen (*vide supra*).

## Remaining Work

- Evaluate computer models and FEFF simulations for the calcium binding site.
- Complete the synthesis and evaluation of the iron vanillin product.
- Prepare chemical models of the Ca binding site.
- Perform the Mn EXAFS.
- Prepare chemical models of the Mn binding site.
- Evaluate iron removal form pulp using several chelating chemicals with very high formation constants for iron.
- Confirm the effect of tightly bound iron on peroxide bleaching.
- Evaluate residual metals partitioning in chlorine dioxide bleaching relative to final pH.

## Conclusions

The EXAFS results suggest that the binding site for tightly bound iron in wood pulp is the 1-hydroxy-2-methoxy group of guaiacol type lignin moieties. Efforts are under way to confirm this analysis. EXAFS spectra have been obtained for calcium in pulp and appear to be suitable for determining the structure of the calcium binding site. Selectivity coefficients have been found to describe the ion exchange behavior of softwood pulp. To adequately describe acid removal of calcium the exponent on protons and undissociated acid groups must be changed from 2 to 0.61. All other cation competitions behave according to theory. Selectivity coefficients for the following metals (all expressed relative to Ca with the exponent on the second metal expressed as an exponent on the selectivity coefficient) are as follows; H ($10^{0.61}$), Na ($1^2$), Mg (3), Mn (1.8), and Ba (1.1).

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## DUES-FUNDED PROJECT SUMMARY

## FY 1997 - 1998

**Project Title**: Production and Quality Improvement of Kraft Pulps

**Project Code**:

**Project Number**: NEW

**PAC**: Chemical Pulping and Bleaching

**Division**: Chemical and Biological Science

**Project Staff**
**Faculty/Senior Staff**: J. Li, E. Malcolm, C. Courchene
**Staff**: Tech. III

**FY 97-98 Budget**: (Initial Work Part of F017)
**Allocated as Matching Funds:** N/A

**RESEARCH LINE/ROADMAP**:

Increase Yield by 10% Absolute / Develop Modified Pulping Process.

**PROJECT OBJECTIVE**:

The objective of this project is to significantly increase pulp yield and improve the strength properties of these higher yield pulps to the level of the market pulp. Initial work will center on suitable polysulfide and PS/catalyst pulping (with or without split sulfidity liquor) and oxygen delignification conditions with respect to chemical concentration and temperature profiles.

**PROJECT BACKGROUND**:

R & D interest and demand in kraft pulp industry have been drastically shifted to reducing production cost and improving product quality, which is very different from dealing with environmental concerns over the bleaching effluents only a few years ago. The most important reason behind such a change is the stiff competition in global marketplace, especially from the low-cost producers in South America and Southeast Asia. In addition, the public concerns on kraft bleaching effluents have been adequately addressed after huge spending on changing to ECF bleaching process and effluent treatment system.

Under the present economical environment, it is unlikely that US pulp and paper industry will have large amount of capital spending. Therefore, the most effective way to reduce production cost is to capitalize on the present digester and recovery capacity by significantly increasing pulp yield. Higher pulp yield can lead to significant production increase because improved pulp yield will off-load the chemical recovery furnace, thus more wood chip can be pulped. The key issue that has to be addressed in obtaining higher yield with various technologies is if the strength properties can be preserved to the level of market pulp or better.

Yield improvement in kraft pulping, where the goal is to remove lignin, is achieved by reducing carbohydrate loss, which is due to a) removal of the end units containing aldehyde groups one by one, the so-called *peeling* reaction; b) dissolution of the lower molecular weight polysaccharides in alkali solution, especially as delignification is extended to lower kappa. Therefore, research efforts in this area have focused on two methods: a) in the past, to find additives to minimize the peeling reaction; b) more recently, stopping the cook at higher kappa, and using oxygen delignification to reduce the residual lignin content.

Cost and compatibility with chemical recovery have allowed only two chemicals, polysulfide (PS) and anthraquinone (AQ), among many pulping additives to reach commercial application [1, 2]. Wider use of polysulfide cooking may be encouraged by the recent invention of the *Paprilox* process, which allows easy, inexpensive production of polysulfide liquors with less capital investment than competing processes [3-5]. Wider use of catalyst cooking will likely increase by the recent research that has led to a lower cost catalyst (dimethylanthraquinone, DMAQ) [6].

Presently, the yield increase from PS and PS/catalyst pulping is limited by the amount of sulfur available in the white liquor for conversion to PS and by catalyst cost. Depending on the polysulfide charge and kappa number, the range of yield gain when employing conventional PS is from 2% for bleachable grade pulp (e.g. 30 kappa number) to 4% for linerboard pulp at 95 kappa number [7]. Factors slowing progress in application of polysulfide pulping are lower tear strength of bleachable grade pulp and low tear and burst strengths of linerboard pulp [1,7]. Lower pulp strength will eventually increase the cost in the down stream operation, e.g. lower paper machine speed or higher usage of strength reinforcement pulp or additives.

To improve polysulphide effectiveness without increasing sulfur load, the multistage polysulphide (MPS) pulping processes were developed [8, 9]. By controlling the cooking chemical concentration, and temperature profiles, MPS pulping doubled the pulp yield gain over that obtained in conventional PS pulping, to 3-4%, without increasing the PS charge on wood, which could lead to production increase more than 10% when the mill is recovery limited. The key technology required to practice MPS pulping is an economically feasible process to split white liquor into sulfide-rich and NaOH liquors, which is expected in the near future as the development of black liquor gasification, green liquor crystallization, or membrane separation technology becomes more advanced. It should be emphasized that there is no major capital required to modify a continuous digester to perform this kind of cook. The major concern on the MPS pulp is again the lower viscosity and tear strength.

The second method to improve pulp yield, high kappa number (40 to 50) pulping followed with extended oxygen delignification, has recently received a lot of interest, since oxygen delignification is more selective in preserving pulp yield than kraft cooking. The pulp yield improvement up to 2% was demonstrated by Jameel et al. [10]. The present process, however, have a significant drawback: the pulp had not only lower tear strength, but also lower tensile strength, which is not economically acceptable. There is no study reported on the yield gain achievable by combining conventional or multi-stage PS pulping with oxygen delignification of high kappa number pulping. Another problem associated with the high kappa number pulping is the high shive content, which cannot be satisfactorily eliminated by an oxygen stage.

As one of the solutions to address the lower viscosity and tear strength problem associated with the MPS pulp, modified multi-stage PS (MMPS) pulping was developed by the researchers at Paprican [11]. The modification extends and intensifies the PS pretreatment, leading to a high sulfidity cooking environment, which improved pulp viscosity by 30%. The tear strength was also improved over that of conventional PS pulp, along with a yield gain twice of that obtained by conventional PS. When this modified multi-stage PS pulping is combined with a newly developed two-stage kraft cooking at Paprican [12], a further improvement in tear strength was achieved. The higher residual alkali concentration used in this two-stage cooking and the other process [13] could also be applied to conventional PS cooking to improve its pulp viscosity and strength. These research results suggest that the strength properties of the higher yield pulp could be improved to the level of the market pulp with proper cooking chemical concentration and temperature profiles. Knowledge developed in these research and process development provides the guidelines to improve pulp strength properties with significantly higher yield.

## EXPERIMENTAL OUTLINE

*Modified Cooking with One Polysulfide Liquor for Bleached Pulp*

Wood chip preparation → Equipment modification and preparation → Reference cooking → Modified one-liquor polysulfide cooking with or without the new catalyst → Oxygen delignification → Physical testing → Report → Internal and PAC review of the progress →

*Modified Cooking with One Polysulfide Liquor for Unbleached Pulp*

Reference cooking of unbleached kraft→ Modified one-liquor polysulfide cooking with or without the new catalyst → Physical testing → Report → Internal and PAC review of the progress →

*Modified Cooking with Split-sulfidity Polysulfide Liquors*

Multistage polysulfide pulping with or without the new catalyst → Oxygen delignification →Report → Internal and PAC review of the progress → Completion report

## SUMMARY OF RESULTS:

Two research proposals on the subjects proposed above, i.e. kraft pulp yield and strength improvement, have been submitted for external research grand application (DOE and Georgia Consortium).

## GOALS FOR FY 97-98:

1. **Complete initial wood chip preparation**: Logs of suitable species, probably southern pine, will be provided by an IPST member company. We will chip these and characterize them at IPST, prior to pulping experiments in our laboratory. The wood chips will be classified. To obtain accurate pulp yield, only the fraction with 2 to 6 mm thickness will be used in the cooking to minimize moisture variation and reject level. The large size fractions will be used in the study of minimizing rejects by optimizing the cooking conditions.

2. **Initiate digester modification**: Upgrading modification of our cooking system to have the capability of liquor displacement and chemical concentration control.

**DELIVERABLES FOR FY 97-98**

Deliverables of this project will include

(1) initial experimental design and wood chip prepared.

(2) complete the design of the new digester system, and start to modify the existing digester.

**SCHEDULE FOR FY 97-98** (beginning April 1998):

| Time (months from start) | Milestone (completion of Indicated Activity) |
|---|---|
| 0 | Arrange for wood supplies |
| 1 | Preparation and characterization of wood chips |
| 3 | Initial modification of existing digester system |

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# DUES-FUNDED REPORTS

# EXTERNAL-FUNDED PROJECT SUMMARY
# FY 1997-98

| | |
|---|---|
| **Project Title:** | SULFUR-FREE SELECTIVE PULPING PROCESS |
| **Project Number:** | 3661 |
| **PAC:** | Chemical Pulping and Bleaching |
| **Division:** | Chemical and Biological Sciences |
| **Project Staff** | |
| **Faculty/Senior Staff:** | Donald Dimmel, Chuck Courchene |
| **Staff:** | Elizabeth Althen |
| | Pulping & Bleaching, Paper Testing, and Analytical Personnel |
| **FY 97-98 Budget:** | Department of Energy funds of $96,000 |
| **Time Allocation** | |
| **Faculty/Senior Staff:** | 40% for 6 months |
| **Support:** | 150% for 6 months |
| **Supporting Research** | |
| **M.S. Students:** | Karen Crews, Kurt Haunreiter, Shawn Reed |

## RESEARCH LINE/ROADMAP:

Environmental Performance:

- Develop economically viable pulping technology to produce kraft equivalent pulp which ensures no odor at mill boundaries.
- Reduce emissions of entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule while maintaining global competitiveness.

## PROJECT OBJECTIVE:

The objective is to develop improved pulping processes by synthesizing and utilizing low-cost catalysts that will increase pulping rates and product yields, while reducing the dependence on sulfur additives. The goal is to prepare a useful quinone-type catalyst that has a cost equivalent to ~$1.00/lb. anthraquinone .

## PROJECT BACKGROUND:

A joint research effort between IPST and the National Renewable Energy Laboratory (NREL) is being conducted on ways to produce cost-effective pulping catalysts. The research has principally centered on preparing 2,6/7-dimethylanthraquinone (DMAQ) from lignin, an inexpensive pulping by-product. The catalysts-from-lignin process involves treating a hardwood lignin with an oxidizing agent to give 2,6-dimethoxybenzoquinone, which is then treated with isoprene to give a mixture of compounds, the principal component of which is DMAQ. The catalyst cost is highly dependent on the yields of the synthesis steps and the oxidant cost. The best oxidant with lignin (and lignin models) is nitrogen dioxide (prepared *in situ* from sodium nitrite) in methanol. The cost of preparing a catalyst mixture containing DMAQ from lignin is ~$3.00/lb., which is roughly twice the current selling price of AQ, but lower than the $4.50/lb. cost at the start of this project.

We have also developed an alternative preparation of DMAQ. Benzoquinone was treated with isoprene at high temperatures to give an isolated 80% yield of a mixture of bis-adducts (Figure 1). These bis-adducts were quantitatively oxidized by base and oxygen to DMAQ. The cost of DMAQ by this procedure depends strongly on the cost benzoquinone; assuming a 90% conversion of phenol or benzene to benzoquinone by reported patents, the cost has been estimated to be ~$1.70/lb. Since DMAQ is twice as active as AQ, the equivalent AQ cost is ~$0.85/lb.

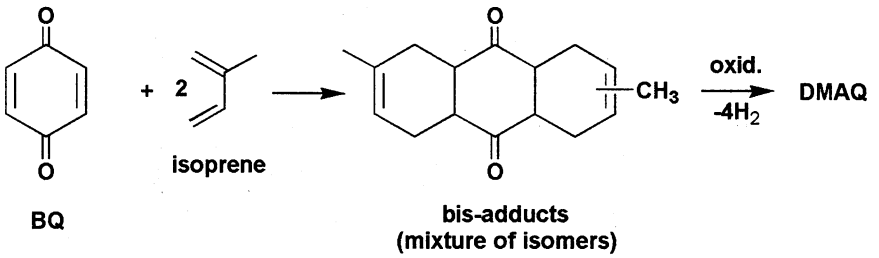


Figure 1. Preparation of DMAQ from Benzoquinone.

## SUMMARY OF RESULTS:

Pulping studies on a 1-Kg scale have confirmed that DMAQ and the bis-adduct mixture are twice as effective as anthraquinone (AQ) in soda, kraft, and polysulfide/catalyst pulping to ~30 kappa pulps. Preliminary comparison cooks targeting higher kappa pulps (50 and 100) indicate no significant advantage of DMAQ vs. AQ. We observed no differences in bleached and unbleached viscosities and in strength properties and brightness levels after full sequence bleaching with D(EOP)DED for DMAQ, bis-adduct, and AQ pulps. The yield improvements for DMAQ, bis-adduct and AQ/kraft pulps are similar.

Analysis of the residual catalyst left on the pulp indicates that the bis-adduct mixture is converted to DMAQ during pulping. The analysis also indicates that there is approximately four times more DMAQ left on the DMAQ and bis-adduct pulps (2% of the applied amount) as there is AQ left (0.5%) on the AQ pulps. This different implies that DMAQ is surviving the cook better than AQ and, thus, could account for its increased effectiveness.

The cost effectiveness of the bis-adduct looks very promising; we are seeking an industrial partner to commercialize the bis-adduct catalyst. A patent has been filed.

Full details of recent research results can be found in a report issued to DOE and to IPST member companies in March 1998.

## FUTURE STUDIES:

The project, which began in the Fall 1988, was terminated in December 1997 with the termination of funding from DOE. New financial support is been sought from the DOE Agenda 2020 program for continued development of bis-adduct catalyst pulping. Joint studies with NREL are not planned. Several student studies are helping to define catalyst performance in extended soda delignification pulping of hardwoods and to assess ways to isolate DMAQ from pulping liquors.

# EXTERNAL-FUNDED PROJECT SUMMARY
# FY 1997-98

**Project Title:** Fundamentals of Lignocellulosic Photostabilization Chemistry

**Project Number:** 4172

**PAC:** Chemical Pulping and Bleaching

**Division:** Chemical and Biological Sciences

**Project Staff**
**Faculty/Senior Staff:** Arthur J. Ragauskas
**Staff:** Cang Li

**FY 97-98 Budget:** USDA New Research Initiative Program - $102,000

**Time Allocation**
**Faculty/Senior Staff:** 8% Ragauskas
**Support:** 100% Li

**Supporting Research**
**Internal:** F014

**RESEARCH LINE/ROADMAP:**

**IMPROVED FOREST PRODUCTIVITY:**

- Develop modified/new pulping/bleaching processes
  - Chemical
  - High yield mechanical strength - high stable brightness
- Use of post treatments to give kraft properties
  - Chemical treatments
  - Mechanical treatments
- Modification of structure or composition of products

**PROJECT OBJECTIVE:**

Develop new technologies to photostabilize high lignin content pulps.

# EXTERNAL-FUNDED PROJECT SUMMARY
# FY 1997-98

**Project Title:** High Efficiency $ClO_2$ Bleaching

**Project Number:** 4159

**PAC:** Chemical Pulping and Bleaching

**Division:** Chemical and Biological Sciences

**Project Staff**
**Faculty/Senior Staff:** Arthur J. Ragauskas/Tom J. McDonough
**Staff:** P. Agrawal

**FY 97-98 Budget:** DOE - $610,000

**Time Allocation**
**Faculty/Senior Staff:** 10% Ragauskas
**Support:** 100% P. Agrawal

**Supporting Research**
**Internal:** F015, Chemical Fundaments of Bleaching
**Students:** T. Runge

**RESEARCH LINE/ROADMAP:**

Environmental Performance:

- Reduce emissions of entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule while maintaining global competitiveness.
- Reduce water usage in bleached kraft pulp production to 2500 gallons per ton.

**PROJECT OBJECTIVE:**

Develop new high efficiency chlorine dioxide delignification technologies.

**SUMMARY:**

See attached publication titled "Fundamental Aspects of Rapid $ClO_2$ Delignification of Conventional and Extended Modified Kraft Pulps."

# EXTERNAL-FUNDED PROJECT SUMMARY
# FY 1997-98

**Project Title:** Low Effluent Pulping/Bleaching Technologies

**Project Number:** 4191

**PAC:** Chemical Pulping and Bleaching

**Division:** Chemical and Biological Sciences

**Project Staff**
**Faculty/Senior Staff:** Arthur J. Ragauskas
**Staff:** Lenong Allison

**FY 97-98 Budget:** Georgia Consortium for Technological Competitiveness - $34,000

**Time Allocation**
**Faculty/Senior Staff:** 5% Ragauskas
**Support:** 10% Allison

**Supporting Research**
**Internal:** -
**Students:** -

**RESEARCH LINE/ROADMAP:**

Environmental Performance:

- Reduce emissions of entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule while maintaining global competitiveness.
- Reduce water usage in bleached kraft pulp production to 2500 gallons per ton.

**PROJECT OBJECTIVE:**

Improved peroxide operations for Georgia's bleaching operations.

**SUMMARY:**

see attached paper titled "A Comparative Evaluation of Low AOX Bleaching Sequences."

# DUES-FUNDED PROJECT SUMMARY
# FY 1997-98

**Project Title:** Fundamentals of Brightness Stability

**Project Number:** F014

**PAC:** Chemical Pulping and Bleaching

**Division:** Chemical and Biological Sciences

**Project Staff**
**Faculty/Senior Staff:** Arthur J. Ragauskas
**Staff:** Lenong Allison

**FY 97-98 Budget:** Private Consortium - $65,000

**Time Allocation**
**Faculty/Senior Staff:** 10% Ragauskas
**Support:** 20% Allison

**Supporting Research**

**RESEARCH LINE/ROADMAP:**

**IMPROVED FOREST PRODUCTIVITY:**

- Develop modified/new pulping/bleaching processes
  - Chemical
  - High yield mechanical strength - high stable brightness
- Use of post treatments to give kraft properties
  - Chemical treatments
  - Mechanical treatments
- Modification of structure or composition of products

**PROJECT OBJECTIVE:**

Project activities are directed at investigating the fundamental chemical reactions that are initiated when high-yield pulp are photolyzed. As our knowledge of the photoxidation of mechanical pulp increases, methods to eliminate or significantly retard the yellowing process will be pursued